



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 629 626 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

27.10.1999 Bulletin 1999/43

(21) Application number: 94304140.0

(22) Date of filing: 08.06.1994

(51) Int Cl. 6: C07D 487/10, C07D 491/107,
C07D 493/10, C07D 495/10,
C07D 209/66, G03C 1/73
// (C07D487/10, 209:00,
209:00),
(C07D491/107, 307:00,
209:00),
(C07D495/10, 333:00, 209:00),
(C07D495/10, 333:00, 307:00)

(54) Cyclopropyl-substituted spiro-photochromic compounds

Cyclopropyl-substituierte Spiro-fotochrome

Composés spirophotochromiques substitués par le groupe cyclopropyl

(84) Designated Contracting States:
DE ES FR IT

• Kobayakawa, Takashi, K.K. Tokuyama
Tokuyama-shi, Yamaguchi-ken 745 (JP)

(30) Priority: 11.06.1993 JP 14102393

(74) Representative: Woods, Geoffrey Corlett et al

J.A. KEMP & CO.

Gray's Inn

14 South Square

London WC1R 5LX (GB)

(43) Date of publication of application:

21.12.1994 Bulletin 1994/51

(56) References cited:
EP-A- 0 316 179

(73) Proprietor: TOKUYAMA CORPORATION
Tokuyama-shi, Yamaguchi-ken 745 (JP)

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

(72) Inventors:

- Imura, Satoshi, K.K. Tokuyama
Tokuyama-shi, Yamaguchi-ken 745 (JP)
- Tanizawa, Tsuneyoshi, K.K. Tokuyama
Tokuyama-shi, Yamaguchi-ken 745 (JP)

EP 0 629 626 B1

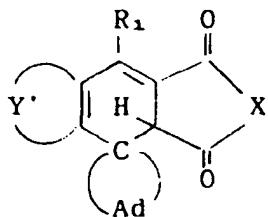
Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] This invention relates to a novel compound having a photochromic action, processes for producing it, a composition comprising it, and to its use. More specifically, it relates to a novel compound having excellent durability which changes reversibly in color from a colorless form to a colored form by the action of light containing ultraviolet rays such as sunlight or the light from a mercury lamp, processes for its production, a composition comprising it, and to its use.

[0002] Photochromism, which has aroused a particular interest for the last several years, denotes a phenomenon in which when light containing ultraviolet rays such as sunlight or the light from a mercury lamp is irradiated onto a certain compound, its color rapidly changes, and when the light irradiation is stopped and the compound is placed in a dark place, its color reversibly returns to the original color. Compounds having this property are called photochromic compounds. Photochromic compounds of various structures have been synthesized and proposed, but no particular common structure has been observed in these compounds.

[0003] Under the circumstances, Japanese Laid-open Patent Application No. 155,179/1985 and the corresponding British Laid-open Patent Application No. 2,146,327 disclose a photochromic compound represented by the following formula



wherein



35 represents an adamantylidene group which may be substituted, R₁ represents hydrogen, an alkyl group, an aryl group, an aralkyl group or a heterocyclic group, X represents oxygen or >NR'₁ in which R'₁ represents hydrogen, an aryl group, an alkyl group or an aralkyl group, and

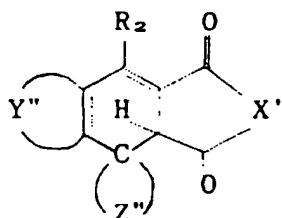


45 represents an aromatic group, an unsaturated heterocyclic group or a heterocyclic group to which a benzene ring is bound, and use of the photochromic compound in a photoreactive lens.

[0004] Japanese Laid-open Patent Application No. 28,154/1990 and the corresponding U.S. Patent No. 4,882,438 describe a fulgide compound or a fulgimide compound represented by the following formula

50

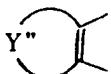
55



10

These compounds are stably colorless in a normal state. However, as soon as they undergo irradiation with sunlight or ultraviolet light, they are colored. When the irradiation stops, they return to the colorless state. These compounds can repeatedly exhibit the color change with good durability and hence, are compounds having excellent photochromic property. In the above fulgide compounds or fulgimide compounds,

15



20

represents an aromatic hydrocarbon group or an unsaturated heterocyclic group, R2 represents a hydrocarbon group or a heterocyclic group, and X' represents an imino group in which a hydrogen atom may be substituted by a specific group, or an oxygen group. Further,

25



30

represents a norbornylidene group or an adamantylidene group which may have a substituent.

[0005] The above fulgide compounds or fulgimide compounds are, as noted above, photochromic compounds which are excellent in durability when a colored form and a colorless form are reversibly repeated. However, development of photochromic compounds having further improved durability has been demanded.

[0006] It is an object of this invention to provide a novel photochromic compound.

35

[0007] Another object of this invention is to provide a compound which reversibly changes from a colorless form to a colored form by the action of ultraviolet rays.

[0008] Still another object of this invention is to provide a photochromic compound having durability which can be used for a long period of time.

[0009] Yet another object of this invention is to provide a photochromic compound having practical utility.

40

[0010] A further object of this invention is to provide industrially advantageous processes for producing the photochromic compound.

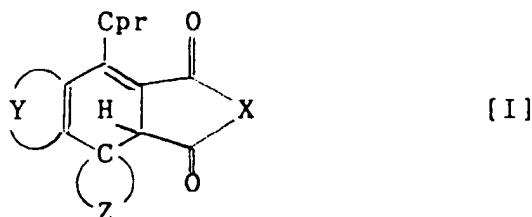
[0011] A still further object of this invention is to provide a polymeric composition comprising the photochromic compound.

[0012] Other objects of the invention will become apparent from the following description.

45

[0013] These objects and advantages of the invention are achieved by a novel compound represented by the following general formula [I]

50



55

wherein

5



represents a divalent aromatic hydrocarbon group or a divalent unsaturated heterocyclic group each of which may
10 have a substituent,

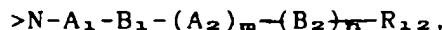
Cpr represents a cyclopropyl group which may have a substituent,

15



represents a norbornylidene group, a bicyclo[3.3.1]nonylidene group, or an adamantylidene group each of which may
have a substituent, and

20 X represents an oxygen atom, the group >N-R₁₁, the group



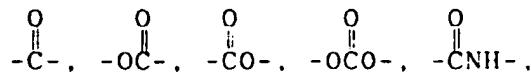
25 the group >N-A₃-A₄, or the group >N-A₃-R₁₃,
in which

R₁₁ represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, or an aryl group having 6 to 10
carbon atoms,

30 A₁ and A₂ are identical or different and each represents an alkylene group having 1 to 10 carbon atoms, an alkyli-
dene group having 2 to 10 carbon atoms, a cycloalkylene group having 3 to 10 carbon atoms or an alkylcycloal-
kanediyl group having 6 to 10 carbon atoms,

B₁ and B₂ are identical or different, and each represents -O-,

35



40 or

45



m and n, independently from each other, represent 0 or 1, provided that when m is 0, n is also 0,

R₁₂ represents an alkyl group having 1 to 10 carbon atoms, a naphthyl group or a naphthylalkyl group having 1 to
50 4 carbon atoms in the alkyl moiety, the alkyl group having 1 to 10 carbon atoms being optionally substituted by 1
to 3 atoms or groups selected from the class consisting of halogen atoms, cyano groups and nitro groups, and the
naphthyl or naphthylalkyl group being optionally substituted by 1 to 3 atoms or groups selected from the class
consisting of halogen atoms, cyano groups, nitro groups, alkylamino groups having 1 to 3 carbon atoms, alkyl
groups having 1 to 3 carbon atoms and alkoxy groups having 1 to 3 carbon atoms,

A₃ represents an alkylene group having 1 to 10 carbon atoms, an alkylidene group having 2 to 10 carbon atoms,
a cycloalkylene group having 3 to 10 carbon atoms, or an alkylcycloalkanediyl group having 6 to 10 carbon atoms,

A₄ represents a naphthyl group which may be substituted by 1 to 3 atoms or groups selected from the class
consisting of halogen atoms, cyano groups, nitro groups, alkylamino groups having 1 to 3 carbon atoms, alkyl
groups having 1 to 3 carbon atoms and alkoxy groups having 1 to 3 carbon atoms, and

R_{13} represents a halogen atom, a cyano group or a nitro group.

- [0014] The compound of the invention represented by general formula [I] will be described below in greater detail.
 [0015] In general formula [I], the group

5



10

represents an aromatic hydrocarbon group or an unsaturated heterocyclic group, which may have at most 5, preferably up to 3, substituents. The aromatic hydrocarbon group has 6 to 20 carbon atoms, preferably 6 to 14 carbon atoms. Examples of the ring forming the aromatic hydrocarbon group are benzene, naphthalene and phenanthrene rings.

[0016] The unsaturated heterocyclic group may be a 5- or 6-membered hetero-monocyclic group containing 1 to 3, preferably 1 or 2, hetero atoms selected from nitrogen, oxygen and sulfur atoms, or a condensed heterocyclic group in which a benzene ring or a cyclohexene ring is fused. Examples of the ring forming these heterocyclic groups are nitrogen-containing heterocyclic rings such as pyrrole ring, a pyridine ring, a quinoline ring, an isoquinoline ring, an imidazole ring and a benzimidazole ring; oxygen-containing heterocyclic rings such as furan ring, a benzofuran ring and a pyrane ring; sulfur-containing heterocycling rings such as a thiophene ring and a benzothiophene ring and rings containing two kinds of hetero atoms such as an oxazole ring and a thiazole ring.

[0017] As stated above, the aromatic hydrocarbon group or unsaturated heterocyclic group represented by

20

25



contains at most 5, preferably up to 3, substituents. Possible the substituents are halogen atoms such as fluorine, chlorine, bromine and iodine; a hydroxyl group; a cyano group; an amino group; a nitro group; a carboxyl group; alkylamino groups having 1 to 4 carbon atoms such as methylamino and diethylamino groups; alkyl groups having 1 to 4 carbon atoms such as methyl, ethyl, propyl and t-butyl groups; halogenated lower alkyl groups containing 1 to 3 halogen atoms such as trifluoromethyl and 2-chloroethyl groups; lower alkoxy groups having 1 to 4 carbon atoms such as methoxy, ethoxy and t-butoxy groups; aryl groups having 6 to 10 carbon atoms such as phenyl, naphthyl and tolyl groups; aryloxy groups containing 6 to 14 carbon atoms such as phenoxy and 1-naphthoxy groups; aralkyl groups having 7 to 15 carbon atoms such as benzyl, phenylethyl and phenylpropyl groups; aralkoxy groups having 7 to 15 carbon atoms such as benzyloxy and phenylpropoxy groups; and alkylthio groups having 1 to 4 carbon atoms. These substituents may be of the same or different kind, and the position of substitution is not particularly limited.

40



is preferably a divalent aromatic hydrocarbon group or a divalent unsaturated heterocyclic groups, each of which may be substituted by at least one atom or group selected from the class consisting of halogen atoms, a nitro group, a cyano group, an amino group, alkylthio groups having 1 to 4 carbon atoms, aryl groups having 6 to 10 carbon atoms, alkyl groups having 1 to 4 carbon atoms and alkoxy groups having 1 to 4 carbon atoms.

[0018] More preferably, it is an aryl group having 6 to 14 carbon atoms, a 5- or 6-membered heteromonocyclic group containing 1 to 3 carbon atoms selected from nitrogen, oxygen and sulfur atoms; or a condensed heterocyclic group resulting from fusion of a benzene or cyclohexene ring to the heterocyclic group, each of which may be substituted by 1 to 3 substituents described above.

50

[0019] Specifically,

55



is preferably a benzene ring or a 5- or 6-membered hetero-monocyclic group containing one hetero atom, or a condensed heterocyclic group resulting from fusion of a benzene or cyclohexene ring with this heterocyclic ring. These

benzene ring, hetero-monocyclic group and condensed heterocyclic ring may preferably contain 1 to 2 substituents described above.

[0020] In general formula [I], Cpr represents a cyclopropyl group which may have a substituent.

[0021] Specific examples of such a substituent are the same as those described in the above formula

5



10 [0022] In general formula [I],

15



is a norbornylidene, a bicyclo[3.3.1]nonylidene or adamantlylidene group which may have a substituent. The norbornylidene group is represented by the following formula

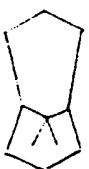
20



25

The bicyclo[3.3.1]nonylidene group is represented by the following formula

30



35

The adamantlylidene group is represented by the following formula

40



45

[0023] The above formulae show the skeletal structures of the norbornylidene group, the bicyclo[3.3.1]nonylidene group and the adamantlylidene group having no substituent. One or more hydrogen atoms in the above formulae may be substituted by a substituent. The types and number of substituents and the substitution positions may be selected according to the purpose and utility. When the norbornylidene, bicyclo[3.3.1]nonylidene or adamantlylidene group has 50 a plurality of substituents, they may be of the same or different kinds.

[0024] Possible substituents for the norbornylidene, bicyclo[3.3.1]nonylidene or adamantlylidene group are a hydroxyl group; alkylamino groups having 1 to 4 carbon atoms such as methylamino and diethylamino groups; alkoxy groups having 1 to 4 carbon atoms such as methoxy, ethoxy and tertbutoxy groups; aralkoxy groups having 7 to 15 carbon atoms such as a benzyloxy group; aryloxy groups having 6 to 14 carbon atoms such as phenoxy and 1-naphthoxy groups; lower alkyl groups having 1 to 4 carbon atoms such as methyl, ethyl and t-butyl groups; halogen atoms such as fluorine, chlorine and bromine atoms; a cyano group; a carboxyl group; alkoxy carbonyl groups having 2 to 10 carbon atoms such as an ethoxycarbonyl group; halogenated alkyl groups having 1 to 2 carbon atoms such as a trifluoromethyl group; a nitro group, aryl groups having 6 to 10 carbon atoms such as phenyl and tolyl groups; and aralkyl groups

having 7 to 9 carbon atoms such as phenylethyl and phenylpropyl groups.

[0025] The halogen atoms, hydroxyl group, alkyl groups having 1 to 4 carbon atoms, alkoxy groups having 1 to 4 carbon atoms, alkoxy carbonyl groups having 2 to 10 carbon atoms, aralkyl groups having 7 to 9 carbon atoms and aryl groups having 6 to 10 carbon atoms are preferred.

5 [0026] In general formula [I] in this invention, X represents an oxygen atom (-O-), the group >N-R₁₁, the group >N-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂, the group >N-A₃-A₄ or the group >N-A₃-R₁₃.

[0027] Preferably, in general formula [I],

10



is a norboonylidene group, a bicyclo[3.3.1]nonylidene group or an adamantylidene group which may have a substituent, and X is the group >N-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂, the group >N-A₃-A₄ or the group >N-A₃-R₁₃, especially the group >N-A₃-R₁₃ or the group >N-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂.

[0028] Preferably, in general formula [I], X is the group >N-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂ and R₁₂ is a naphthyl or naphthylalkyl group, or X is the group >N-A₃-A₄, the number of atoms in the main chain interposed between the naphthyl group and the imide group >N- is 3 to 7 because it leads to a compound having durable photochromism.

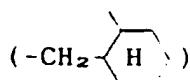
20 [0029] Now, the definitions of R₁₁, R₁₂, R₁₃, A₁, A₂, A₃, A₄, B₁, B₂, m and n in X will be described.

[0030] R₁₁ represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, or an aryl group having 6 to 10 carbon atoms. Examples of the alkyl group are methyl, ethyl, n-, iso- or tert-butyl, pentyl, hexyl, octyl and decyl groups. Those having 1 to 10 carbon atoms are preferred. Examples of the aryl group are phenyl, tolyl and naphthyl groups.

25 [0031] A₁ and A₂ may be identical or different, and each may represent an alkylene group having 1 to 10 carbon atoms, an alkylidene group having 2 to 10 carbon atoms, a cycloalkylene group having 3 to 10 carbon atoms, or an alkylcycloalkanediyl group having 6 to 10 carbon atoms. Specific examples of the alkylene groups are methylene, ethylene, propylene, butylene, trimethylene, tetramethylene and 2,2-dimethyltrimethylene groups. Specific examples of the alkylidene groups are ethylidene, propylidene and isopropylidene groups. A cyclohexylene group may be cited

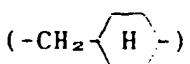
30 as the example of the cycloalkylene groups. Examples of the alkylcycloalkanediyl groups are 2-methylcyclohexane- α , 1-diyli

35



and 4-methylcyclohexane- α ,1-diyli

40



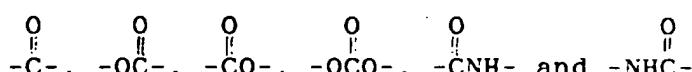
45

groups. The alkylene groups having 1 to 6 carbon atoms, the alkylidene groups having 2 to 6 carbon atoms, the cycloalkylene groups having 3 to 6 carbon atoms, and the alkylcycloalkanediyl groups having 6 to 7 carbon atoms are preferred as A₁ and A₂.

[0032] B₁ and B₂ may be identical or different, and each is selected from the following seven bridging groups.

[0033] -O-,

50



55

[0034] m and n, independently from each other, represent 0 or 1. When they represent 0, -(A₂)_m- or -(B₂)_n means a bond. When m is 0, n is also 0.

[0035] R₁₂ represents an alkyl group having 1 to 10 carbon atoms, a naphthyl group, or a naphthylalkyl group having

1 to 4 carbon atoms in the alkyl moiety. The alkyl group having 1 to 10 carbon atoms may be substituted by 1 to 3 atoms or groups selected from the class consisting of halogen atoms, a cyano group and a nitro group. The naphthyl and naphthylalkyl groups may be substituted by 1 to 3 atoms or groups selected from the class consisting of halogen atoms, a cyano group, a nitro group, alkylamino groups having 1 to 3 carbon atoms, alkyl groups having 1 to 3 carbon

5 atoms and alkoxy groups having 1 to 3 carbon atoms. Examples of the alkyl groups having 1 to 10 carbon atoms may be the same as those given with regard to the alkyl groups for R₁₂. Examples of the naphthylalkyl group are naphthylmethyl, naphthylethyl, naphthylpropyl and naphthylbutyl groups.

[0036] A₃ represents an alkylene group having 1 to 10 carbon atoms, an alkylidene group having 2 to 10 carbon atoms, a cycloalkylene group having 3 to 10 carbon atoms, or an alkylcycloalkanediyl group having 6 to 10 carbon atoms. Specific examples of the alkylene, alkylidene, cycloalkylene and alkylcycloalkanediyl groups may be the same as those given with regard to A₁ and A₂ above.

[0037] A₄ represents a naphthyl group which may be substituted by 1 to 3 atoms or groups selected from the class consisting of halogen atoms, cyano groups, nitro groups, alkylamino groups having 1 to 3 carbon atoms, alkyl groups having 1 to 3 carbon atoms and alkoxy groups having 1 to 3 carbon atoms.

[0038] R₁₃ represents a halogen atom, a cyano group or a nitro group.

[0039] In the definitions of R₁₂, R₁₃ and A₄, the halogen atom may be, for example, fluorine, chlorine or bromine.

[0040] In this invention, preferred examples of the compound represented by the general formula [I] are as follows.

(1) 4-cyclopropyl-6,7-dihydrido-N-methoxycarbonylmethylspirobenzo[5,6-b]thiophenedicarboxyimido-7,7'-bicyclo[2.2.1]heptane

(2) N-cyanomethyl-4-cyclopropyl-6,7-dihydridospirobenzo[5,6-b]thiophenedicarboxyimido-7,7'-bicyclo[2.2.1]heptane

(3) 2-bromo-4-cyclopropyl-6,7-dihydrido-N-(β-naphtylethyl)spirobenzo[5,6-b]thiophenedicarboxyimido-7'9'-bicyclo[3.3.1]nonane

(4) 2-bromo-4-cyclopropyl-6,7-dihydridospirobenzo[5,6-b]thiophenedicarboxyanhydride-7,2'-tricyclo[3.1.1^{3,7}]decane

(5) 4-cyclopropyl-6,7-dihydrido-2-methyl-N-nitromethylspirobenzo[5,6-b]thiophenedicarboxyimide-7,7'-bicyclo[2.2.1]heptane

(6) 4-(2"-methylcyclopropyl)-6,7-dihydrido-N-methylcarbonylmethyl-2-phenylspirobenzo[5,6-b]-thiophenedicarboxyimido-7,7'-bicyclo[2.2.1]heptane

(7) 3,4-dihydro-5,7-dimethoxy-N-(O-naphthylmethyl)-1-(2",3"-tetramethylcyclopropyl)-spirophthalenedicarboxyimido-4,7'-bicyclo[2.2.1]heptane

(8) N-cyanomethyl-6,7-dihydro-4-(2-phenoxy)cyclopropylspirobenzo[6,5-b]furancarboxyimido-7,7'-bicyclo[2.2.1]heptane

(9) 2-bromo-4-(2",3"-dichloromethyl)-6,7-dihydro-N-isobutoxycarbonylmethylspirobenzo[5,6-b]thiophenecarboxyimido-7,9'-bicyclo[3.3.1]nonane

(10) 6-cyclopropyl-8,9-dihydrospirodibenzo-[5,6-b:d]thiophenecarboxyanhydride-9,7'-bicyclo-[2.2.1]heptane

(11) 4-cyclopropyl-6,7'-1,2-dimethylspiroindolecarboxyanhydride-7,9'-bicyclo[3.3.1]nonane

(12) 2-bromo-4-cyclopropyl-3',3"-dimethylspirobenzo[5,6-b]thiophenecarboxyimido-7,9'-bicyclo[3.3.1]nonane

(13) 2-bromo-7-cyclopropyl-4,5-dihydro-N-methylcarboxymethylspirobenzo[5,6-b]thiophenecarboxyimido-4,2-tricyclo[3.3.1.1^{3,7}]decane

(14) 1,2,3,4,8,9-hexahydro-N-(α-naphthylpentyl)-6(2"-methylcyclopropyl)spirodibenzo[5,6-b:d]thiophenecarboxyimido-9,2'-tricyclo[3.3.1.1^{3,7}]decane

(15) 4-cyclopropyl-6,7-dihydrido-2-nitrospirobenzo[5,6-b]thiophenedicarboxyanhydride-7,2'-tricyclo[3.3.1.1^{3,7}]decane

[0041] The compound of the general formula [I] generally exists as a pale yellow solid at room temperature, and can generally be identified by the following procedures (a) to (c).

50 (a) The types and number of protons existing in the molecule can be determined by measuring the proton nuclear magnetic resonance spectrum (¹H-NMR) of the compound. Specifically, in the ¹H-NMR spectrum, there appears a peak based on aromatic protons near δ7-8 ppm, a broad peak based on protons derived from the cyclopropyl, adamantylidene, bicyclo[3.3.1]nonylidene or norbornylidene group near δ1.2-2.5 ppm. By comparing the δ peak intensities of these peaks, the number of protons of the bonding groups can be determined.

55 (b) By elemental analysis, the weight percentages of carbon, hydrogen, nitrogen, sulfur and halogen can be determined. The weight percent of oxygen can be calculated by subtracting the total weight percentage of the elements from 100. Accordingly, the composition of the product can be determined.

(c) The types of carbons present in the molecule can be determined by measuring the ¹³C-nuclear magnetic res-

onance spectrum of the compound. There appear a peak derived from carbons of the cyclopropyl, adamantlylidene, bicyclo[3.3.1]nonylidene or norbornylidene group near δ 27-52 ppm, a peak based on the carbons of the aromatic hydrocarbon group or the unsaturated heterocyclic group near δ 110-150 ppm, and a peak based on the carbon of $>\text{C}=\text{O}$ near δ 160-170 ppm.

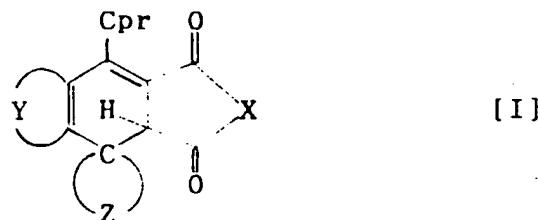
5

[0042] The compound of general formula [I] may be produced by any manufacturing process, and is not limited by the type of manufacturing process. Preferred typical processes are described below without any intention of limiting the invention thereby.

10 Process A

[0043] A process for producing a compound represented by the following general formula [I]

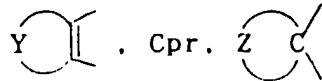
15



20

25 wherein

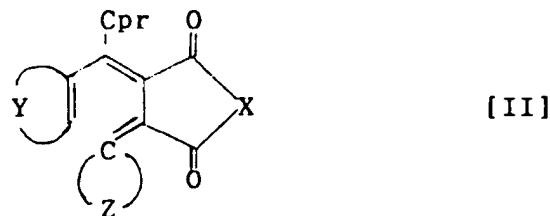
26



30

and X are as defined hereinabove,
which comprises cyclizing a compound represented by the following general formula [II]

35



40

45 wherein

50

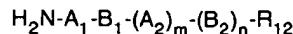
and X are as

defined with regard to general formula [I], or reacting the compound of general formula [II] with an amine compound represented by the following general formula [III-a], [III-b], [III-c] or [III-d]

55



[III-a]

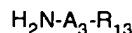


[III-b]

5



[III-c]



[III-d]

10

wherein R_{11} , R_{12} , R_{13} , A_1 , A_2 , A_3 , A_4 , B_1 , B_2 , m and n are as defined above, and then cyclizing the reaction product.

15

[0044] A compound of general formula [I] in which X is an oxygen atom is obtained by cyclizing the acid anhydride of general formula [II] in process A. Compounds of general formula [I] containing an imide ring in which X is other than oxygen can be obtained by reacting the acid anhydride of general formula [II], with the amine compound of formula [III-a], [III-b], [III-c] or [III-d], and then cyclizing the resulting product.

20

[0045] The reaction in process A is carried out preferably in a solvent. The solvent may be an aprotic polar solvent such as N-methylpyrrolidone, dimethylformamide, tetrahydrofuran or 1,4-dioxane.

25

[0046] The direct cyclization of the acid anhydride of general formula [II] and the cyclization of the reaction product of the acid anhydride with the amine compound can be carried out under the same conditions. The cyclization is carried out, for example, by heating the compound to a temperature of 160 to 220°C, or carrying out this heating with ultraviolet irradiation, or by bringing the compound into contact with a Lewis acid catalyst. The Lewis acid catalyst may be a known compound such as SnCl_4 , TiCl_4 , SbCl_5 and AlCl_3 . The amount of the Lewis acid used is not particularly restricted, but usually amounts of 0.001 to 1 mole per mole of the compound to be cyclized are preferred.

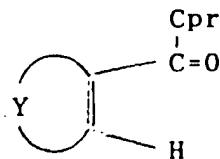
30

[0047] In the reaction of the acid anhydride of general formula [II] with the amine compound of general formula [III-a], [III-b], [III-c] or [III-d], the mole ratio of the acid anhydride to the amine compound can be varied over a wide range, but is generally from 1:10 to 10:1, preferably from 1:5 to 5:1. This reaction is carried out usually at a temperature of 25 to 160°C for a period of 1 to 24 hours. After the reaction, the solvent is removed, and the product is dehydrated with a dehydrating agent such as acetyl chloride and acetic anhydride. By cyclizing the resulting compound under the conditions described above, the compound [I] of the invention can be obtained.

35

[0048] The acid anhydride of general formula [II] used as the starting material in process A can be obtained, for example, by condensing a carbonyl compound represented by the following general formula [II-a]

35



[II-a]

40

wherein

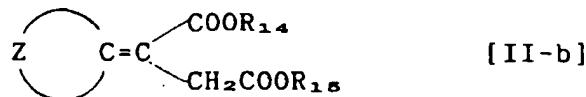
45



50

and Cpr are as defined with regard to general formula [I], with a succinic diester derivative represented by the following general formula [II-b]

55



[II-b]

wherein



is as defined in general formula [I], and R₁₄ and R₁₅ are identical or different and represent an alkyl group having 1 to 6 carbon atoms,

and treating the resulting product in a manner described below.

10 [0049] The mole ratio of the carbonyl compound to the succinic diester derivative in the above condensation reaction may be varied over a wide range, and is generally from 1:10 to 10:1, preferably 1:5 to 5:1. The reaction is carried out at a temperature of 0 to 110°C, preferably 10 to 100°C. The reaction is suitably carried out in a solvent. The solvent is desirably an aprotic solvent such as benzene, diethyl ether, toluene and tetrahydrofuran.

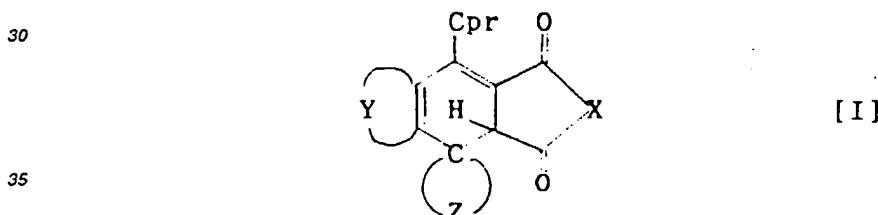
15 [0050] Generally, the condensation is carried out in the presence of a condensing agent such as sodium hydride, potassium t-butoxide and sodium ethylate. The condensing agent may be used usually in an amount of 0.1 to 10 moles per mole of the carbonyl compound of general formula [II-a].

[0051] After the reaction, the resulting dicarboxylic acid diester is converted to the free dicarboxylic acid. This reaction is carried out by using known hydrolysis reaction conditions in the presence of bases. For example, the reaction is carried out at 0 to 80°C using a 10 % ethanolic aqueous solution of sodium hydroxide.

20 [0052] The resulting dicarboxylic acid can be converted to the acid anhydride of general formula [II] by known methods. conversion into the acid anhydride may be carried out, for example, by using a well known reagent such as acetic anhydride or acetyl chloride.

Process B

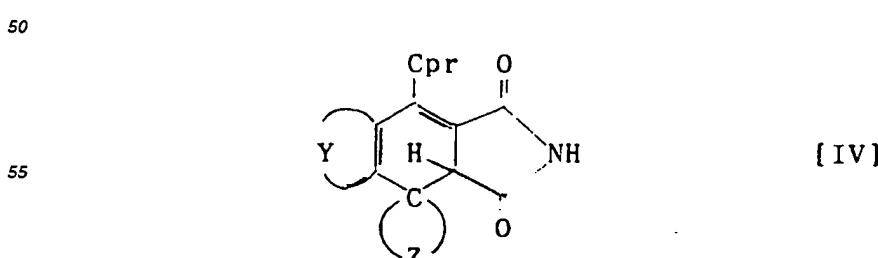
25 [0053] A process for producing a compound represented by the following general formula [I]



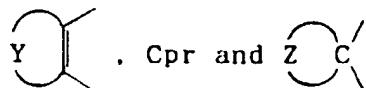
wherein

40

45 and X are as defined with regard to general formula [I], provided that an oxygen atom is excluded from the above definition of X,
which comprises reacting an imide compound represented by the following general formula [IV]

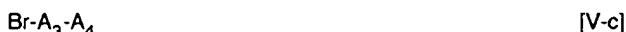


5 wherein



are as defined with regard to the general formula [I],

10 with an alkali metal, and then reacting the product with a bromine compound represented by the following general formula [V-a], [V-b], [V-c] or [V-d]



25 wherein R_{11} , R_{12} , R_{13} , A_1 , A_2 , A_3 , A_4 , B_1 , B_2 , m and n are as defined with regard to the general formula [I].

30 [0054] Examples of the alkali metal used in process B are sodium, potassium, and lithium. The amount of the alkali metal to be reacted is generally 1.0 to 10 moles per mole of the compound of general formula [IV]. Preferably, the amount of the bromine compound of general formula [V-a], [V-b], [V-c] or [III-d] is generally 0.5 to 10 moles per mole of the compound [IV] obtained by reaction with the alkali.

[0055] The solvent used in this process may be any of those which are described above with regard to process A. Usually, the reaction temperature used may preferably be 0 to 100°C. The compound of general formula [I] of the invention can be obtained by the above processes A and B or by modifications of these processes.

[0056] The compound of general formula [I] has a photochromic action and excellent durability. By using it in combination with an ultraviolet stabilizer, the durability of the photochromic action of compound [I] can be further enhanced.

35 [0057] Accordingly, it is advantageous to use the compound [I] of the invention in combination with an ultraviolet stabilizer.

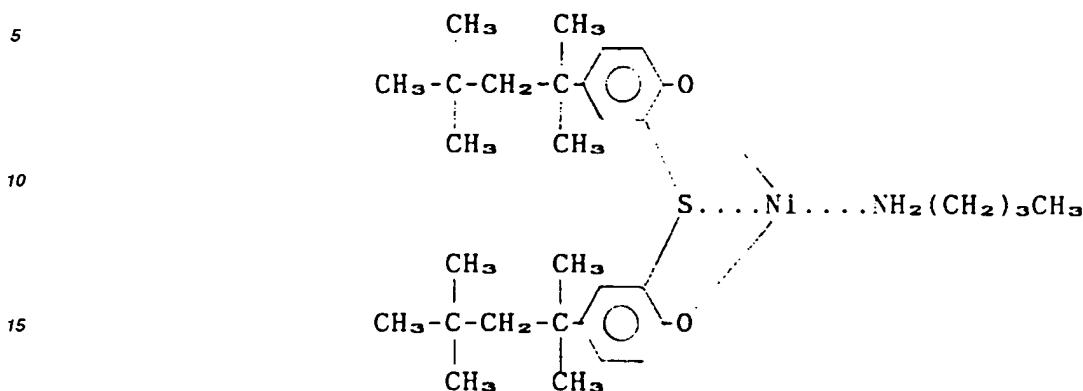
[0058] The ultraviolet stabilizer used for this purpose may be any of those known as additives to various plastics. If the durability of the compound [I] is considered, light extinguisher for oxygen in the singlet state and hindered amine light stabilizers can be suitably used as the ultraviolet stabilizer.

40 [0058] Examples of light extinguisher for oxygen in the singlet state which can be suitably used in this invention include a complex of Ni^{2+} and an organic ligand, cobalt (III) tris-di-n-butylthiocarbamate, iron (III) diisopropylthiocarbamate and cobalt (II) diisopropylthiocarbamate. The complex of Ni^{2+} and an organic ligand is especially preferred. Examples of this complex are shown below.

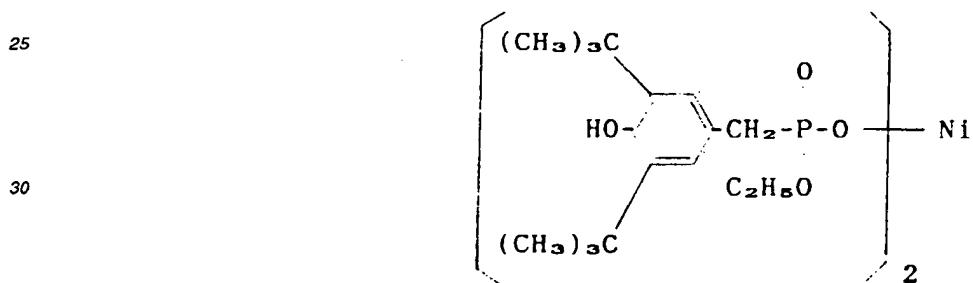
45

50

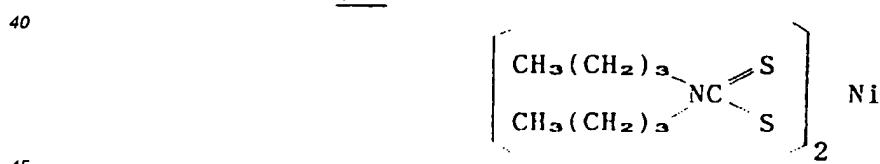
55

U-1

20 [0059] [2,2'-thiobis-4-(1,1,3,3-tetramethylbutyl)phenolate]butylamine]nickel

U-2

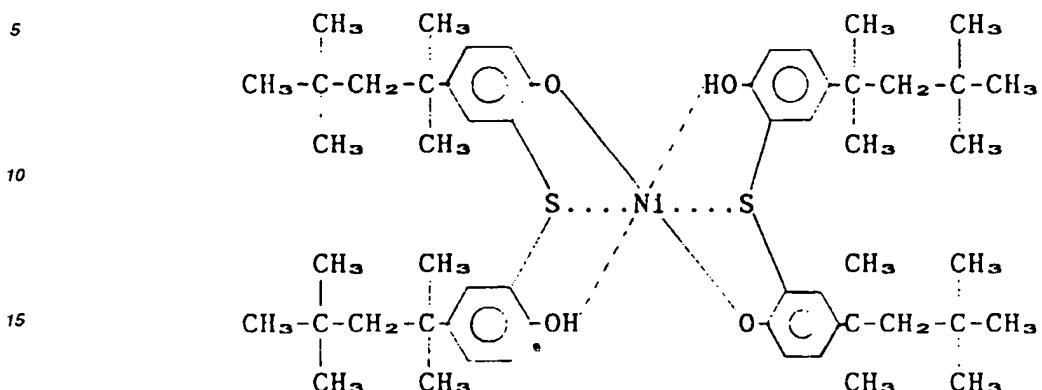
[0060] Nickel-bis[o-ethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate]

U-3

[0061] Nickel dibutyl dithiocarbamate

50

55

U-4

- [0062] bis[2,2'-thiobis-4-(1,1,3,3-tetramethylbutyl)phenolate]nickel
- [0063] There may also be cited Ni complexes sold by Ferro Corporation under the tradenames UV-Chek AM105, UV-Chek AM126 and UV-Chek AM205.
- [0064] Specific examples of the hindered amine light stabilizers suitable as the ultraviolet stabilizer are given below.

25

U-5

30

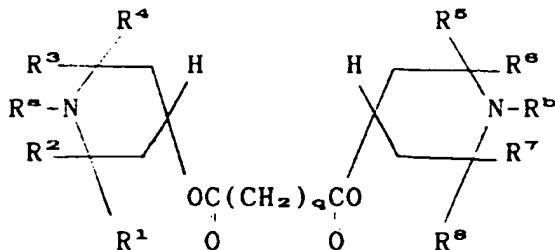
35

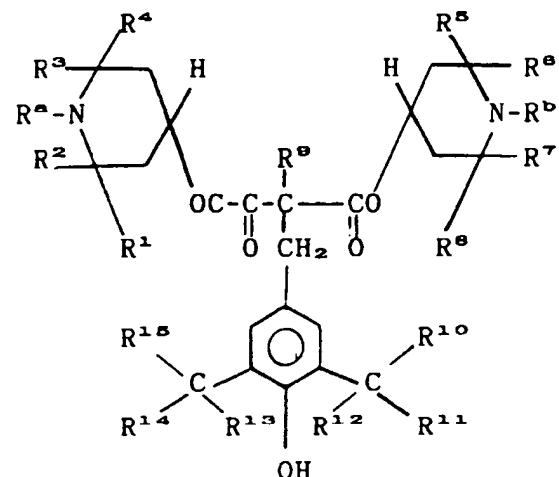
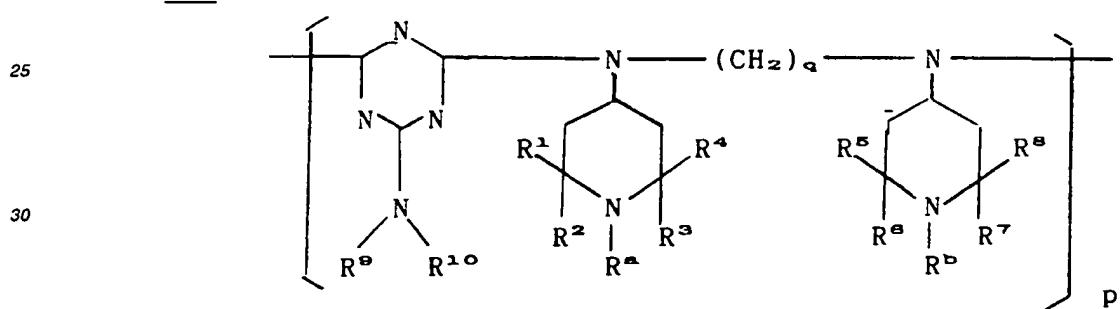
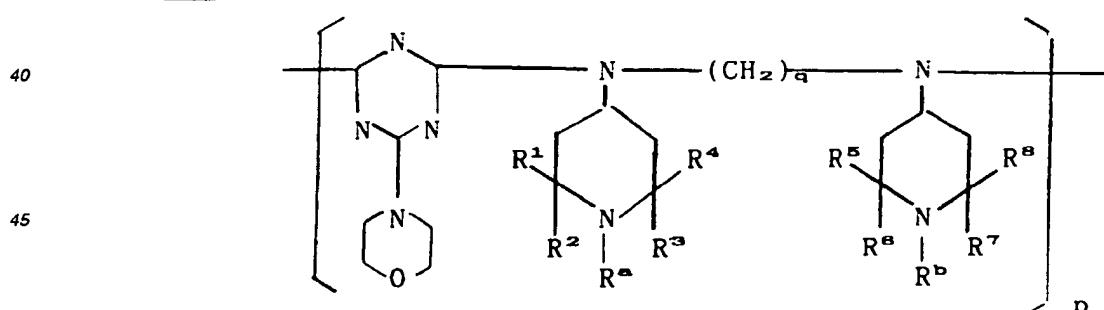
40

45

50

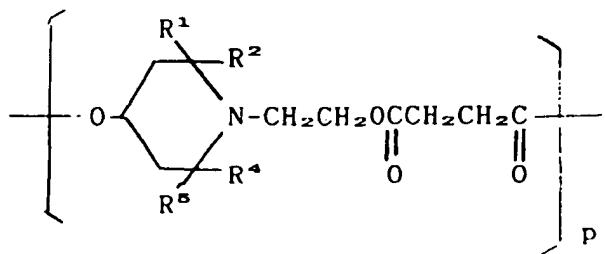
55



U-6U-7U-8

55

U-9



5

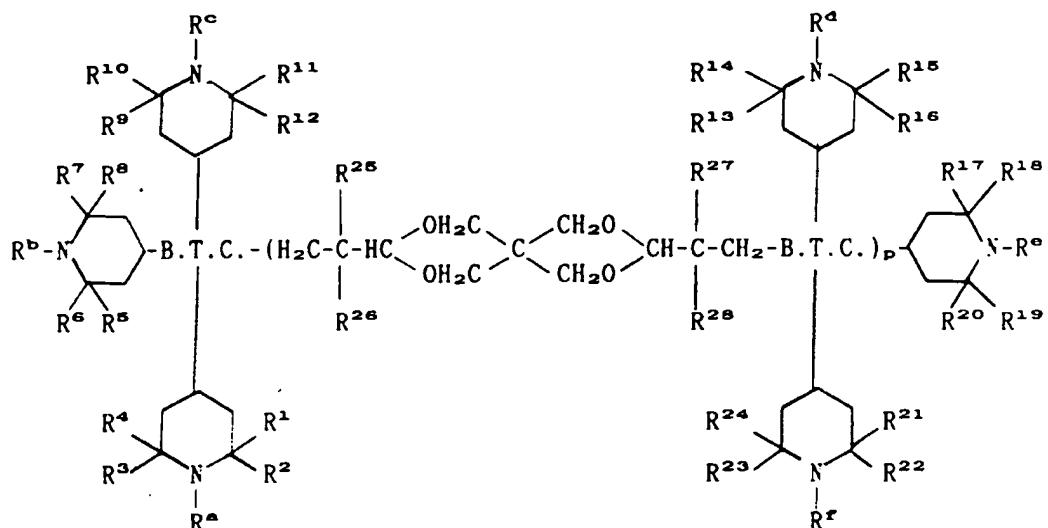
10

15

U-10 $(C_{26}H_{52}N_4)_p$

U-11

20

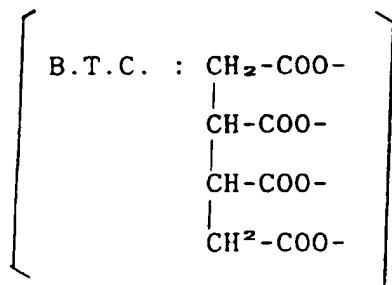


40

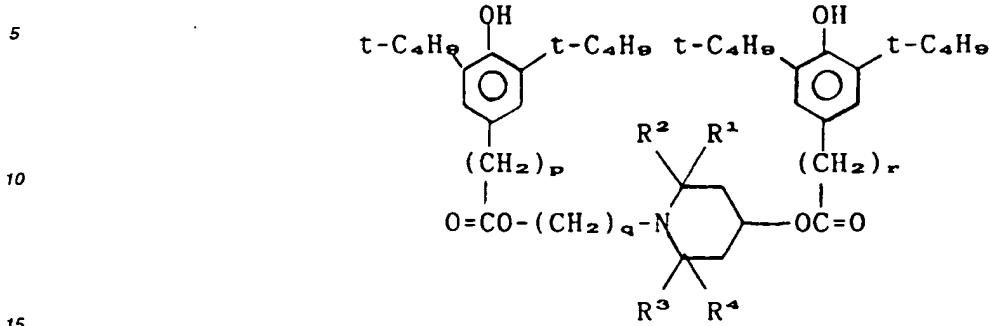
45

50

55



U-12



[0065] In the formulae, U-5 to U-12, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷ and R²⁸ represent an alkyl group, R^a, R^b, R^c, R^d, R^e and R^f represent a hydrogen atom or an alkyl group, and p, q and r are positive integers.

20 [0066] The alkyl groups in U-5 to U-12 are not particularly limited in the number of carbons. Generally, the alkyl groups preferably have 1 to 12 carbon atoms because of the ease of obtaining these compounds.

[0067] Sumisorb LS-2000 and LS-2001 (tradenames of Sumitomo Chemical Co., Ltd.) may also be cited as examples of the hindered amine light stabilizer.

25 [0068] Ultraviolet stabilizers of formulae U-1, U-3, U-5, U-6, U-8, U-9, U-11 and U-12 can be preferably used for increasing the durability of the photochromic actions of the compounds of general formula [I].

[0069] The mixing ratio of the compound of formula [I] and the ultraviolet stabilizer can be selected from a wide range. Generally, if the durability of a composition of the compound [I] and the ultraviolet stabilizer and the prevention of dissolution of the components, the proportion of the ultraviolet stabilizer is generally 0.01 to 10,000 parts by weight, more preferably 50 to 400 parts by weight, per 100 parts by weight of compound [I].

30 [0070] The compound of general formula [I] provided by this invention is well soluble in general organic solvents such as toluene, chloroform and tetrahydrofuran. When the compound [I] is dissolved in such a solvent, the solution has a reversible photochromic action such that it is almost colorless and transparent, and when sunlight or ultraviolet rays are irradiated onto it, it develops a color, and when the light is shut off, it rapidly attains the original colorless form.

35 [0070] The compound of general formula [I] also exhibits this photochromic action in a polymeric solid matrix with a reversing speed on the order of seconds. A high-molecular-weight polymer for forming such a polymeric material may be any polymer in which the compound [I] is dispersible uniformly. The molecular weight of the high-molecular-weight polymer is selected from 500 to 500,000. Any of thermoplastic resins and thermosetting resins may be adopted as the polymer solid material.

40 [0071] The thermoplastic resins include, for example, polymethyl acrylate, polyethyl acrylate, polymethyl methacrylate, polyethyl methacrylate, polystyrene, polyacrylonitrile, polyvinyl alcohol, polyacrylamide, poly(2-hydroxyethyl-methacrylate), polydimethylsiloxane and polycarbonate.

[0072] Dispersion of the compound represented by the general formula [I] of the present invention into a thermoplastic resin can be carried out by the synthesis of the thermoplastic, that is, the polymerization or melting and mixing the thermoplastic resin and the compound at temperature not less than a melting point of the thermoplastic resin.

45 [0073] The thermosetting resins include the polymers of radical polymeric multifunctional monomers which include, for example, polyvalent acrylate and polyvalent methacrylate compounds such as ethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, ethylene glycol bisglycidyl methacrylate, bisphenol A dimethacrylate, 2,2-bis(4-methacryloyloxyethoxyphenyl)propane, 2,2-bis(3,5-diboromo-4-methacryloyloxyethoxyphenyl)propane; polyvalent allyl compounds such as diallyl phthalate, diallyl terephthalate, diallyl isophthalate, diallyl epoxy succinate, diallyl fumarate, diallyl chlorendate, diallyl hexaphthalate, diallyl carbonate, allyl diglycol carbanate, trimethylolpropane triallyl carbonate; polyvalent thioacrylate and polyvalent thiomethacrylate compounds such as 1,2-bis(methacryloylthio)ethane, bis(2-acryloylthioethyl)ether, 1,4-bis(methacryloylthiomethyl)benzene; methacrylate or acrylate compounds such as glycidyl acrylate, glycidyl methacrylate, β -methylglycidyl methacrylate, β -methylglycidyl acrylate, bisphenol A-monoglycidylether methacrylate, 4-glycidyloxybutyl methacrylate, 3-(glycidyloxy-1-isopropoxy)-2-hydroxypropyl acrylate, 3-(glycidyloxy-2-hydroxypropoxy)-2-hydroxypropyl acrylate; and divinylbenzene. The thermosetting resins may also include, for example, copolymers of the radical polymeric multifunction monomers with radical polymeric monofunctional monomers including unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic anhydride; acrylate and methacrylate compounds such as methyl acrylate,

methyl methacrylate, benzyl methacrylate, phenyl methacrylate, 2-hydroxyethyl methacrylate; fumarate compounds such as diethyl fumarate, diphenyl fumarate; thioacrylate and thiomethacrylate compounds such as methylthioacrylate, benzyl thioacrylate, benzyl thiomethacrylate; and vinyl compounds such as styrene, chlorostyrene, methylstyrene, vinylnaphthalene and bromostyrene. The thermosetting resins may further include addition copolymers of the above-

5 mentioned radical polymeric multifunctional monomers with polyvalent thiol compounds such as ethanedithiol, propanethiol, hexanodithiol, pentaerythritol tetrakis(thioglycolate), di(2-mercaptoethyl)ether; and addition copolymers of polyvalent isocyanate compounds such as diphenylethane diisocyanate, xylene diisocyanate, p-phenylene diisocyanate with polyvalent alcohol compounds such as ethylene glycol, trimethylolpropane, pentaerythritol, bisphenol A on the above-mentioned polyvalent thiol compounds.

10 [0074] Dispersion of the compound of the general formula [I] into the thermosetting resin may be generally carried out by mixing the starting monomers of the thermosetting resin with the compound of the general formula [I] and thereafter polymerizing them.

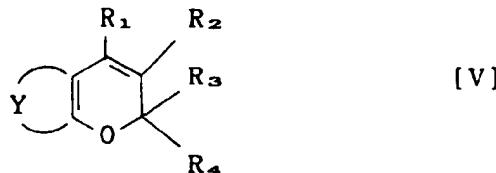
15 [0075] The amount of the compound [I] to be dispersed in the above high-molecular polymer is generally 0.001 to 70 parts by weight, preferably 0.005 to 30 parts by weight, especially preferably 0.1 to 15 parts by weight, per 100 parts by weight of the high-molecular polymer. When the ultraviolet stabilizer is used by mixing it with the high-molecular polymer, its amount may be within the range of the mixing proportion with respect to the compound [I] described above.

20 [0076] The photochromic action of the compound of general formula [I] has much higher durability than known fulgide compounds.

25 [0077] Accordingly, the compounds of this invention can be broadly utilized as a photochromic material. For example, they can be utilized in various recording materials superseding silver salt photographic materials, for example, in memory materials, printing photographic materials, recording materials for a cathode ray tube, photographic materials for laser and photographic materials for holography. The photochromic material containing the compound of this invention can also be utilized as a photochromic lens material, an optical filter material, a display material, an actinometer or a decorative material. For example, a photochromic lens may be produced by any method which can give uniform light adjusting properties. Specifically, a polymer film in which the photochromic compound of this invention is uniformly dispersed in sandwiched between lenses. Alternatively, a photochromic lens may be produced by dissolving the compound of the invention in a silicone oil, impregnating the solution in the surface of a lens at 150 to 200°C over 10 to 60 minutes, and coating the surface with a curable substance. It is also possible to coat the above polymer film on the surface of a lens and coating the surface with a curable substance to provide a photochromic lens. A photochromic lens may also be produced by dispersing the compound of the invention in monomers capable of forming an organic lens, and then polymerizing and curing the monomeric mixture.

30 [0078] When the photochromic compound is used as an photochromic lens, a color such as grey or brown is preferred. Since such a single photochromic compound cannot give such a color, a method of mixing two or more photochromic compounds may be adopted. The compound of general formula [I] is generally colored in orange to blue. When it is mixed with the chromene compound which is colored in yellow to orange, an intermediate color such as grey and brown may be obtained. Generally, fulgide compound has a poor durability of photochromic properties as compared with chromene compound, and changes may occur in color with the lapse of time. For this reason, a mixed color of the fulgide compound and the chromene compound changes with time. However, in accordance with this invention, by increasing the durability of photochromism of the fulgide compound, it is made close to the durability of the chromene compound, and a divergence in color with the lapse of time can be minimized.

35 [0079] The chromene compound preferably used in admixture with the compound of general formula [I] to obtain an intermediate color may be represented by formula [V].



wherein R₁, R₂, R₃ and R₄ are the same or different, and each represents a hydrogen atom, an alkyl group, an aryl group, a substitution amino group or a saturated heterocyclic group, R₃ and R₄ may together form a ring, and the group

55



is a divalent aromatic hydrocarbon group or a divalent unsaturated heterocyclic group each of which may have a substituent.

[0080] Examples of the alkyl and aryl groups represented by R_1 , R_2 , R_3 and R_4 in formula [V] may be the alkyl and aryl groups described above with regard to formula [I]. Examples of the substituted amino group may be amino groups whose at least one hydrogen atom is substituted by the aforesaid alkyl or aryl group. Examples of the saturated heterocyclic group include monovalent groups derived from 5- to 6-membered rings containing 1 to 2 ring-constituting atoms such as nitrogen atoms, oxygen atoms and sulfur atoms such as a pyrrolidine group, an imidazolidine ring, a piperidine ring, a piperazine ring and a morpholine ring.

[0081] Examples of the ring formed by R_3 and R_4 in formula [V] include a norbornylidene group and a bicyclo[3.3.1]nonylidene group.

[0082] The aromatic hydrocarbon group or the unsaturated heterocyclic group represented by



15

in formula [V] may be the same as those shown in formula [I]. Substituents of these groups are not particularly limited. Examples of the substituents include halogen atoms such as chlorine, bromine and iodine, alkyl groups having 1 to 20 carbon atoms such as methyl group and an ethyl group, alkoxy groups having 1 to 20 carbon atoms such as a methoxy group and an ethoxy group, aryl groups having 6 to 10 carbon atoms such as a phenyl group, a tolyl group and a xylol group, amino groups, a nitro group and a cyano group.

[0083] Examples of the chromene compounds preferably used in this invention include those of formula [V] in which R_1 and R_2 are both hydrogen atoms, and R_3 and R_4 are same or different alkyl groups having 1 to 4 carbon atoms, or together may form a bicyclo[3.3.1]nonylidene group or a norbornylidene group,

25



30

is a naphthalene ring which may be substituted by an alkyl group having 1 to 20 carbon atoms or an alkoxy group having 1 to 20 carbon atoms.

[0084] The chromene compounds that can be used preferably in this invention are listed below.

- (1) Spiro(norbornane-2,2'-(2H)benzo(h)-chromene)
- (2) Spiro(bicyclo[3.3.1]nonane-9,2'-(2H)benzo(f)-chromene)
- (3) 7'-methoxyspiro(bicyclo[3.3.1]nonane-9,2'-(2H)benzo(f)-chromene)
- (4) 7'-methoxyspiro(norbornane-2,2'-(2H)benzo(f)-chromene)
- (5) 2,2-dimethyl-7-octoxy(2H)benzo(f)-chromene
- (6) 4'-methylspiro[bicyclo[3.3.1]nonane-9,2'-(2H)benzo(f)-chromene]
- (7) 3'-methylspiro[norbornane-2,2'-(2H)benzo(f)-chromene]
- (8) Spiro[tricyclo[3.3.1.13.7]decane-2,2'-(2H)benzo(h)chromene]
- (9) 4'-piperidinospiro[bicyclo[3.3.1]nonane-9,2'-(2H)benzo(h)chromene]
- (10) 2,2-dimethyl-6-octadecyl[2H]benzo(h)chromene
- (11) spiro[norbornane-2,2'-(2H)naphtho[1,2-h]chromene]
- (12) 2,2-dimethyl-7-(ethylthiohexyl)oxy[2H]benzo(h)chromene
- (13) 6-chloro-2,2-dimethyl-7-(dipropylphosphonohexyl)oxy[2H]benzo(h)chromene
- (14) 2,2-dimethyl[2H]pyrido[2,3-h]chromene
- (15) 7-methoxy-2,2-dimethyl[2H]benzo(h)chromene
- (16) 7-(diethylaminoctyl)-2,2-dimethyl-[2H]benzo(h)chromene

50

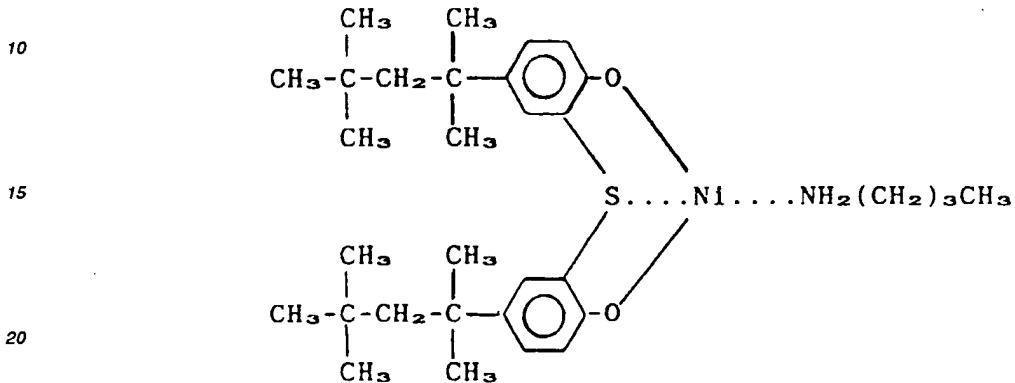
[0085] The mixing ratio of the compound of formula [I] and the chromene compound can be selected from a wide range. Generally, the proportion of the chromene compound is generally 0.01 to 10,000 parts by weight, more preferably 0.05 to 200 parts by weight, per 100 parts by weight of the compound [I].

55

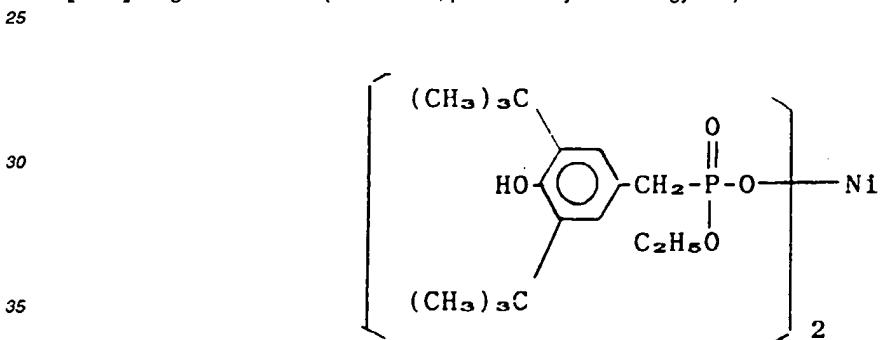
[0086] Compared to the conventional compounds, the compound of general formula [I] in this invention shows markedly improved durability by the effect of the cyclopropyl group, and is longer in maximum absorption wavelength of color form. Further, the compound of general formula [I] wherein X is an oxygen atom is quite increased in color density in comparison to the conventional compounds.

Brief Description of the Drawings

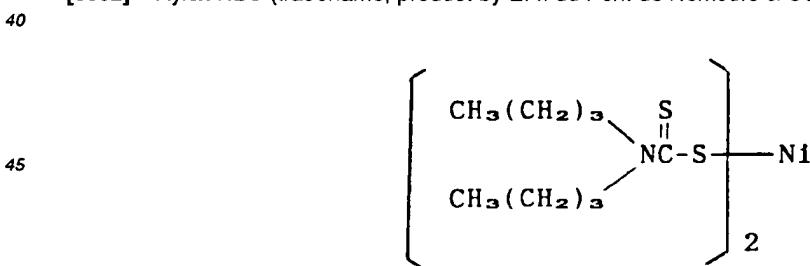
- [0087] Figure 1 is the proton nuclear magnetic resonance spectrum of the product obtained in Example 1.
 [0088] The following examples illustrate the present invention in greater detail without limiting the invention thereby.
 5 [0089] In the examples, the following ultraviolet stabilizers were used.
 [0090] Cyasorb UV1084 (tradename; product of American Cyanamid Co.)



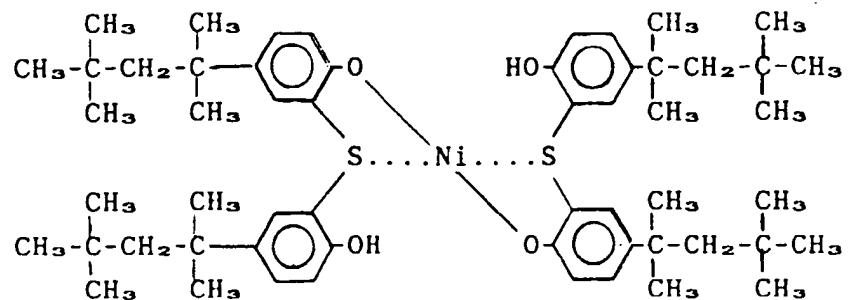
- [0091] Irganostab 2002 (tradename; produced by Ciba-Geigy Co.)



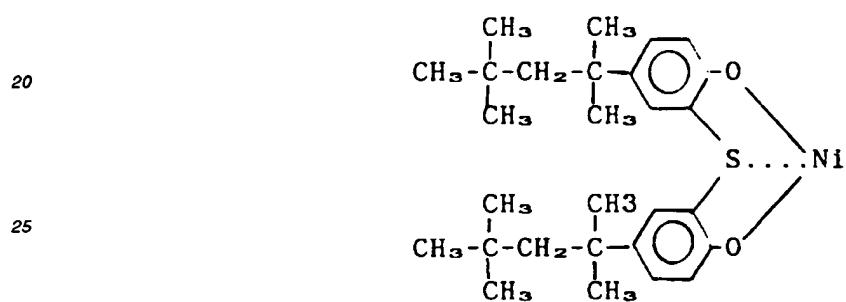
- [0092] Rylex NBC (tradename; product by E. I. du Pont de Nemours & Co.)



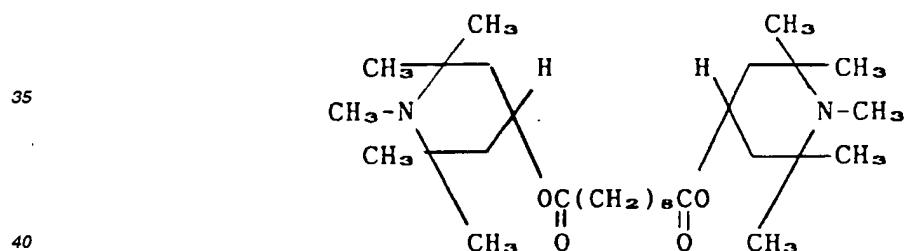
- [0093] UV-Chek AM101 (tradename; produced by Ferro Corporation)



15 [0094] UV-Chek AM105 (tradename; produced by Ferro Corporation)



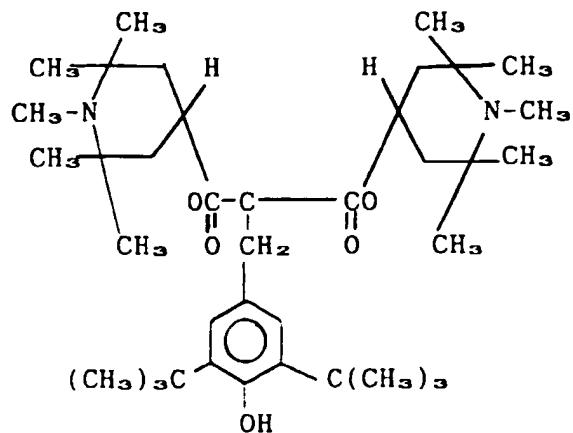
30 [0095] Tinuvin 765 (tradename; produced by Ciba-Geigy Co.)



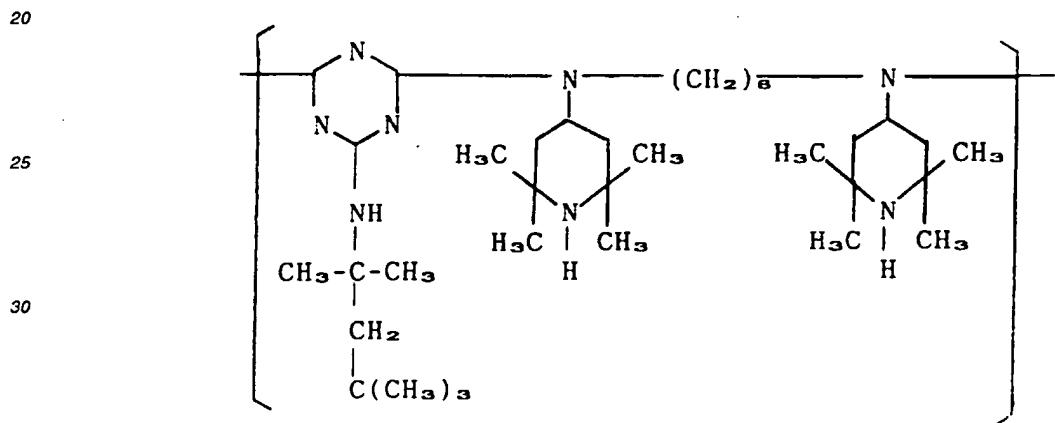
45 [0096] Tinuvin 144 (tradename; produced by Ciba-Geigy Co.)

50

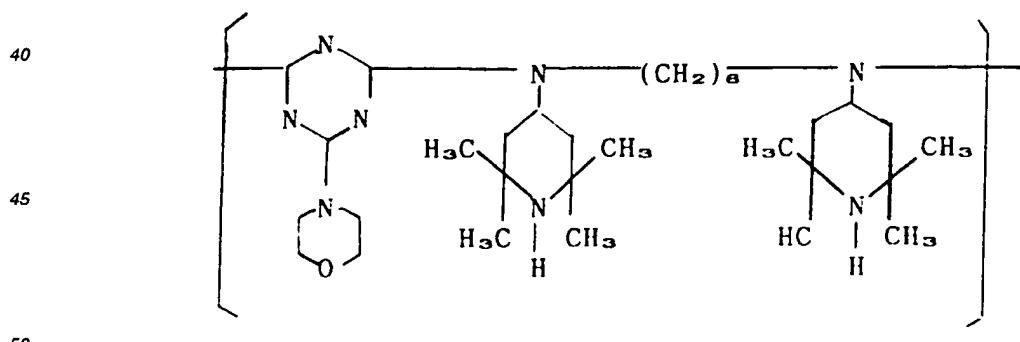
55



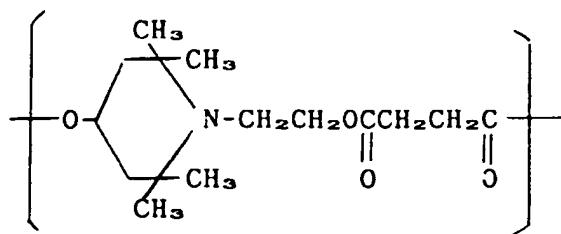
[0097] Chimasorb 944 (tradename; produced by Ciba-Geigy Co.)



[0098] Cyasorb 3346 (tradename; produced by American Cyanamid Co.)



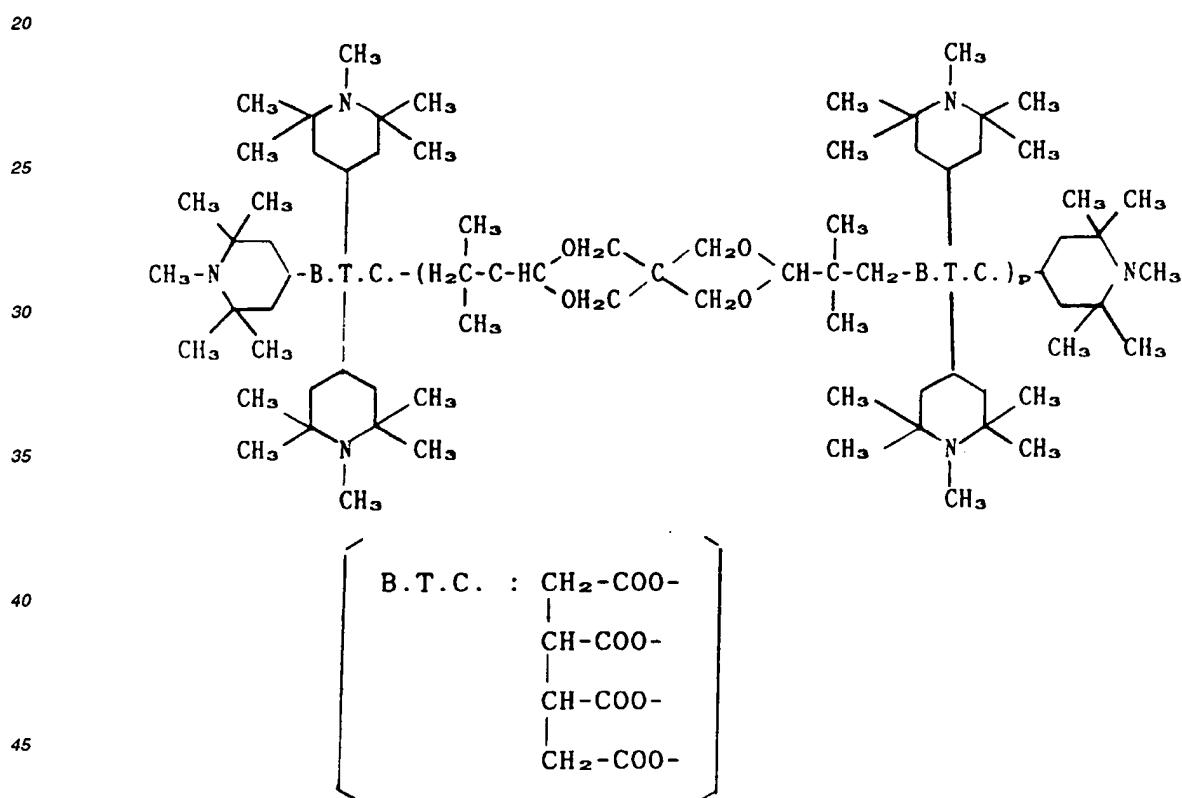
[0099] Tinuvin 622 (tradename; produced by Ciba-Geigy Co.)



[0100] Spinuvex A-36 (tradename; produced by Borg Warner Corp.)



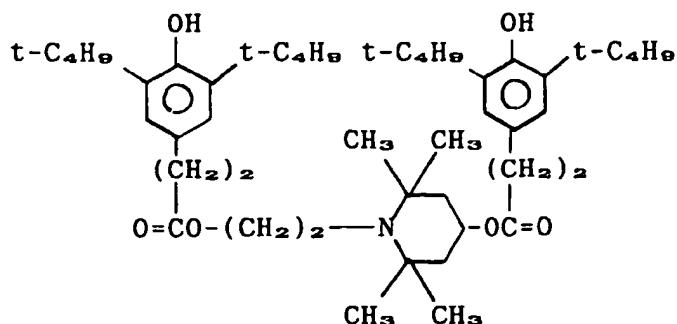
[0101] LA-63 (tradename; produced by Adeca-Agas Corp.)



[0102] LS-2626 (tradename; produced by Sankyo Co.)

50

55



15 [0103] In the Example, the following chromene compound were mentioned.

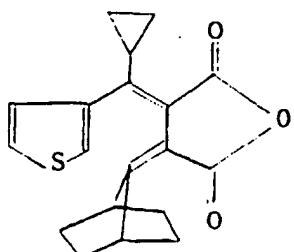
- (1) Spiro(norbornane-2,2'-(2H)benzo(h)-chromene)
 (2) 7'-methoxyspiro(bicyclo[3.3.1]nonane-9,2'-(2H)benzo(f)-chromene)
 20 (3) 4'-methylspiro[bicyclo[3.3.1]nonane-9,2'-(2H)benzo(f)chromene]
 (4) 3'-methylspiro[norbornane-2,2'-(2H)benzo-[f]chromene]
 (5) 2,2-dimethyl-7-octoxy[2H]benzo[h]chromene

25 [0104] The compounds produced in Examples 1 to 7 are referred to as compounds (1) to (7) respectively.

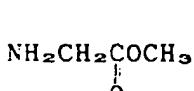
EXAMPLE 1

[0105] 3.3 g (0.01 mole) of cyclopropyl-3-thienylmethylidene-7-norbornylidene succinic anhydride of the following formula

30



and 17.8 g (0.02 mole) of glycine methyl ester of the following formula



50 were dissolved in toluene, and the solution was heated at 50°C for 2 hours in a nitrogen atmosphere. After the reaction, the solvent was removed, and the residue was dissolved in acetyl chloride. The solution was refluxed for 1 hour to cyclize the reaction product. The resulting compound was refluxed for 6 hours in o-dichlorobenzene to convert it into a compound of formula [I]. This compound was purified by chromatography on a silica gel column using benzene and ether as an eluent. Recrystallization from chloroform and hexane gave pale yellow needles in a yield of 23 %. The 55 elemental analysis values of this compound were C 66.52 %, H 5.86 %, N 3.49 %, O 16.3 % and S 8.11 %, which well agreed with the calculated values for C20H21O4NS (C 66.48 %, H 5.83 %, N 3.52 %, O 16.1 % and S 8.07 %). The proton nuclear magnetic resonance spectrum of the resulting compound was taken and shown in Figure 1. The proton nuclear magnetic resonance spectrum of the resulting compound showed a peak of 2H based on aromatic protons

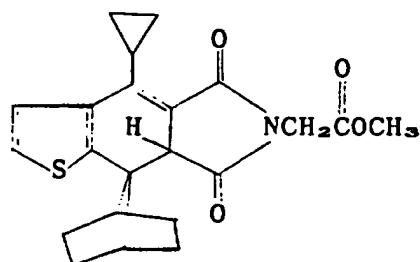
near δ 7.0-8.0 ppm, a peak of 3H based on the methyl protons of the



bond near δ 3.7 ppm, a peak of 15H based on the protons of the cyclopropyl group and the 7-norbornylidene group at δ 1.2-2.5 ppm, and a peak of 3H based on the 1-5 shifted proton and the $>\text{N}-\text{CH}_2-$ bond at δ 3.5 ppm.

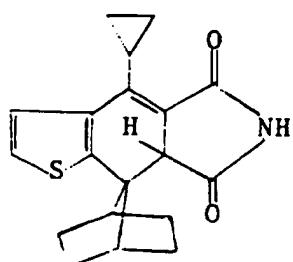
10 [0106] The ^{13}C -NMR spectrum of the resulting product was measured. It showed a peak based on the carbons of the 7-norbornylidene group and the carbon of the methylene chain at δ 27-70 ppm, a peak based on the carbon of the cyclopropyl group near δ 9.7 ppm, and a peak based on the carbons of the thiophene ring near δ 110-160 ppm, and a peak based on the carbon of the $>\text{C}=\text{O}$ bond near δ 160-170 ppm.

15 [0107] From the above results, the isolated products was determined to be a compound of the following structural formula

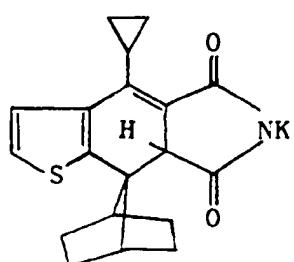


EXAMPLE 2

30 [0108] 3.0 g (0.01 mole) of a compound of the following formula



45 was dissolved in tetrahydrofuran, and then reacted with 1 g of metallic potassium at room temperature to give 3.0 g of potassium imide of the following formula

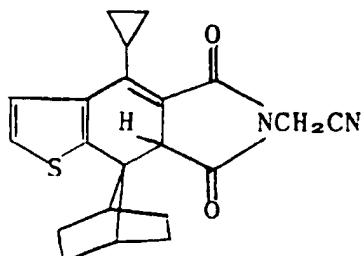


[0109] This compound was reacted with 1.2 g (0.01 mole) of bromoacetonitrile BrCH_2CN in dimethylformamide to give a fulgimide compound shown below. This compound was purified by chromatography on silica gel using chloroform and hexane as an eluent and was obtained in a field of 52 % as pale yellow crystals by recrystallization from hexane. This compound had the following elemental analysis values: C 69.25 %, H 5.55 %, N 7.71 %, O 8.75 % and S 8.90 %.

5 These values well agreed with the calculated values for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ (C 69.21%, H 5.53%, N 7.69%, O 8.78% and S 8.8%). The proton nuclear magnetic resonance spectrum of the resulting compound was measured. The spectrum showed a peak of 2H based on aromatic protons of thiophene ring near δ 7.0-7.5 ppm, a peak of 2H based on the protons of $>\text{N-CH}_2\text{CN}$ bond near δ 4.5 ppm, a peak of 1H based on the 1-5 shifted proton near δ 3.7 ppm, and a peak of 12H based on the protons of the cyclopropyl group and the 7-norbornylidene group at δ 1.3-2.5 ppm.

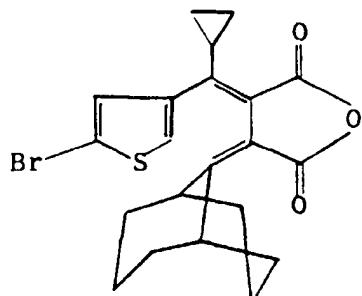
10 [0110] The $^{13}\text{C-NMR}$ of the resulting compound was also measured. The spectrum showed a peak based on the carbons of the 7-norbornylidene group near δ 27-70 ppm, a peak based on the cyclopropyl carbon near δ 10.2 ppm, a peak based on the carbons of the thiophene ring near δ 110-160 ppm, and a peak based on the carbon of $>\text{C=O}$ bond near δ 160-170 ppm.

15 [0111] From the above results, this isolated product was determined to be a fulgimide compound of the following structural formula

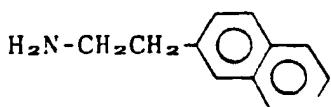


EXAMPLE 3

30 [0112] 4.3 g (0.01 mole) of the following compound



45 and 3.5 g (0.02 mole) of 2-naphthylethylamine of the following formula

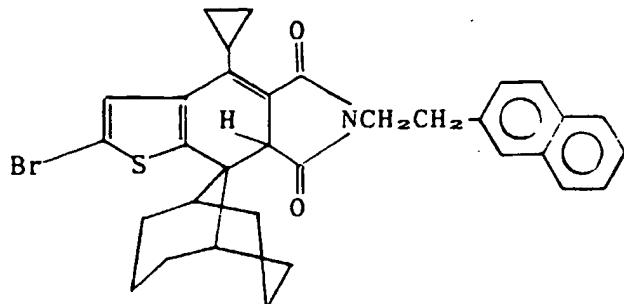


were dissolved in toluene, and heated at 50°C for 2 hours in an atmosphere of nitrogen. After the reaction, the solvent was removed, and the residue was dissolved in acetyl chloride, and refluxed for 1 hour to cyclize the product obtained above. The resulting compound was refluxed for 6 hours in o-dichlorobenzene to form a compound shown below. The 55 compound was purified by chromatography on silica gel using benzene and ether as an eluent. By recrystallization from chloroform and hexane, it was obtained as yellow needles in a yield of 25 %. The elemental analysis values of this compound were C 67.61 %, H 5.52 %, Br 13.65 %, N 2.39 %, O 5.50 % and S 5.41 %, which well agreed with the calculated values for $\text{C}_{31}\text{H}_{30}\text{BrNO}_2\text{S}$ (C 67.57 %, H 5.5 %, Br 13.62 %, N 2.39 %, O 5.46 % and S 5.47 %). The proton

nuclear magnetic resonance spectrum of the resulting compound was measured. The spectrum showed a peak of 8H based on aromatic protons near δ 7.0-8.0 ppm, a peak of 3H based on the 1-5 shifted proton and based on the protons of $>\text{N-CH}_2$ near δ 3.8 ppm, and a peak of 23H based on the protons of the -CH₂- bond and the protons of the cyclopropyl group and the bicyclo[3.3.1]9-nonylidene group near δ 1.3-2.5 ppm.

5 [0113] The ¹³C-NMR spectrum of the resulting product was also measured. It showed a peak based on the carbons of the bicyclo[3.3.1]9-nonylidene group and the carbon of the methylene chain at δ 27-52 ppm, a peak based on the carbon of the cyclopropyl group near δ 9.70 ppm, a peak based on the carbons of the naphthalene ring and the carbons of the thiophene ring near δ 110-160 ppm, and a peak based on the carbon of the $>\text{C=O}$ bond near δ 160-170 ppm.

10 [0114] From the above results, the isolated products was determined to be a fulgimide compound of the following structural formula

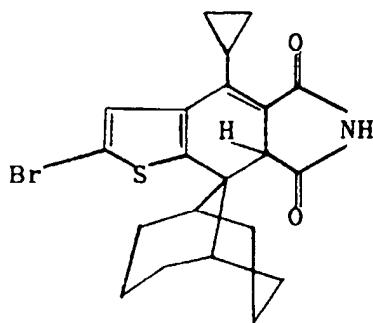


25

EXAMPLE 4

[0115] A fulgimide compound of the following structural formula was obtained by repeating Example 3 except that NH₃ was used instead of 2-naphthylethylamine.

30

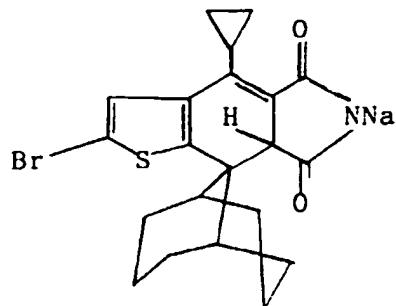


45

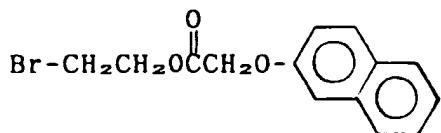
[0116] 6.5 g (0.015 mole) of this compound was dissolved in tetrahydrofuran, and reacted with metallic sodium at room temperature to give 5.4 g of an imide sodium of the following formula

50

55



[0117] This compound was reacted with 2 g (0.01 mole) of 2-bromomethyl 2-naphthoxyacetate of the following formula



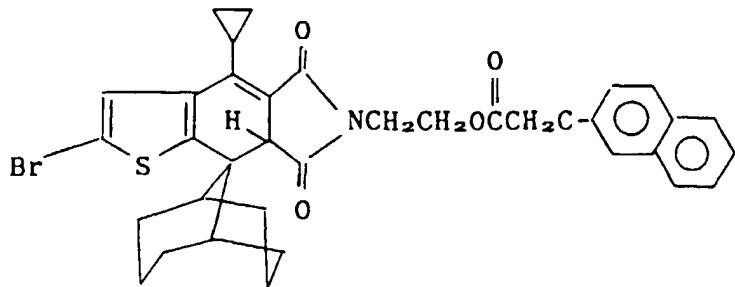
25 in dimethylformamide to give a fulgimide compound shown below. This compound was purified by chromatography on silica gel using chloroform and hexane as an eluent, and from hexane, it was obtained as yellow needles in a yield of 47 %.

[0118] The resulting compound had elemental analysis values of C 63.67 %, H 5.21 %, Br 12.15 %, N 2.15 %, O 12.15 % and S 4.90 %, which well agreed with the calculated values for C₃₃H₃₁BrNO₅S (C 63.63 %, H 5.19 %, Br 12.1 %, N 2.12 %, O 12.11 % and S 4.85 %).

[0119] The proton NMR spectrum of the resulting compound was measured. The spectrum showed a peak of 8H based on aromatic protons near δ7.0-8.0 ppm, a peak of 7H based on the protons of the -CH₂- bond and the 1-5 shifted proton near δ3.0-5.0 ppm, and a peak of 14H based on the cyclopropyl group and the bicyclo[3.3.1]9-nonylidene group at δ1.0-2.2 ppm.

[0120] The ¹³C-NMR spectrum of the resulting product was also measured. The spectrum showed a peak based on the carbons of the bicyclo[3.3.1]9-nonylidene group and the carbon of the methylene chain at δ27-52 ppm, a peak based on the carbon of the cyclopropyl group near δ9.7 ppm, a peak based on the carbon of the thiophene ring and the carbons of the naphthalene ring near δ110-160 ppm, and a peak based on the carbon of the >C=O bond near δ160-170 ppm.

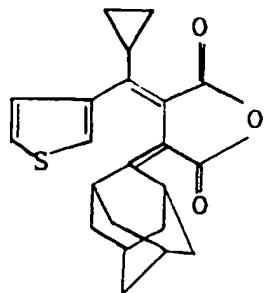
[0121] From the above results, the isolated products was determined to be a fulgimide compound of the following structural formula



55

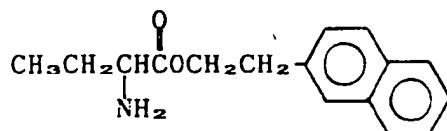
EXAMPLE 5

[0122] 3.7 g (0.01 mole) of cyclopropyl-3-thienylmethylidene succinic anhydride of the following formula



and 2.1 g (0.02 mole) of 2-naphthylethyl 2-aminobutyrate of the following formula

15



were dissolved in toluene, and heated at 50°C for 2 hours in an atmosphere of nitrogen. After the reaction, the solvent was removed, and the residue was dissolved in acetyl chloride and refluxed for 1 hour to cyclize the above reaction product. The resulting compound was refluxed for 6 hours in o-chlorobenzene to form a fulgimide compound of the following structure. This compound was purified by chromatography on silica gel using benzene and ether as an eluent. By recrystallization from chloroform and hexane, it was obtained as yellow needles in a yield of 29 %.

25

[0123] The elemental analysis values of the resulting compound were C 76.65 %, H 5.00 %, N 2.30 %, O 10.75 % and S 5.43 %, which well agreed with the calculated values for $C_{33}H_{33}O_4NS$ (C 76.62 %, H 4.91 %, N 2.35 %, O 10.74 % and S 5.38 %).

30

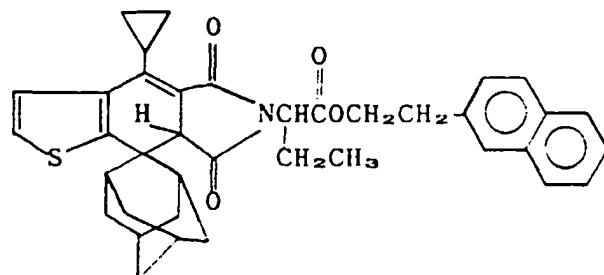
[0124] The proton NMR spectrum of the resulting compound was measured. The spectrum showed a peak of 9H based on aromatic protons near δ 7.0-8.0 ppm, a peak of 3H based on the protons of the methyl group in the $-CH_2CH_3$ bond at δ 0.8-1.2 ppm, a peak of 12H based on protons of the $-CH_2-$ bond and the cyclopropyl group and adamantlylidene group at δ 1.2-2.5 ppm, and a peak of 7H based on the 1-5 shifted proton and the $-CH_2-$ bond at δ 3-5 ppm.

35

[0125] The ^{13}C -NMR spectrum of the resulting product was also measured. The spectrum showed a peak based on the carbons of the adamantlylidene group and the carbon of the methylene group at δ 27-52 ppm, a peak based on the carbon of the cyclopropyl group near δ 9.7 ppm, a peak based on the carbons of the thiophene group and the carbons of the naphthyl group near δ 110-160 ppm, and a peak based on the carbon of the $>C=O$ bond near δ 160-170 ppm.

40

[0126] From the above results, the isolated products was determined to be a fulgimide compound of the following structural formula



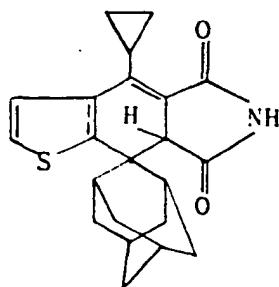
55

EXAMPLE 6

[0127] 3.5 g (0.01 mole) of a fulgimide compound of the following formula

5

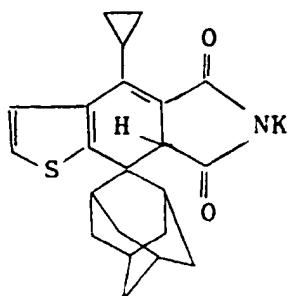
10



was dissolved in tetrahydrofuran, and reacted with 1 g of metallic potassium at room temperature to give 3.0 g of imide potassium of the following formula

20

25



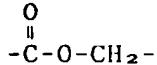
30 The resulting compound and 1.8 g (0.01 mole) of 2-naphthylethyl 5-bromo-
35 valerate of the following formula

40 were reacted in dimethylformamide to give a fulgimide compound shown below. This compound was purified by chromatography on silica gel using chloroform and hexane as an eluent. By recrystallization from hexane, it was obtained as yellow crystals in a yield of 63 %.

[0128] The elemental analysis values of the resulting compound were C 75.91 %, H 5.35 %, N 2.41 %, O 10.91 % and S 5.50 %, which well agreed with the calculated values for $C_{34}H_{35}NO_4S$ (C 75.87 %, H 5.33 %, N 2.39 %, O 10.93 % and S 5.47 %).

[0129] The proton NMR spectrum of the resulting compound was measured. The spectrum showed a peak of 9H based on aromatic protons near 87.0-8.0 ppm, a peak of 2H based on the protons of the

50



55 bond near 84.4 ppm, a peak of 3H based on the 1-5 shifted proton and protons of the >N-CH2- bond near 83.7 ppm, a peak of 27H based on the protons of -CH2- bond and the protons based on the cyclopropyl group and adamantlylidene group at 81.3-2.5 ppm.

[0130] The ^{13}C -NMR spectrum of the resulting product was also measured. The spectrum showed a peak based on the carbons of the adamantlylidene group and the carbon of the methylene chain at 827-52 ppm, a peak based on the

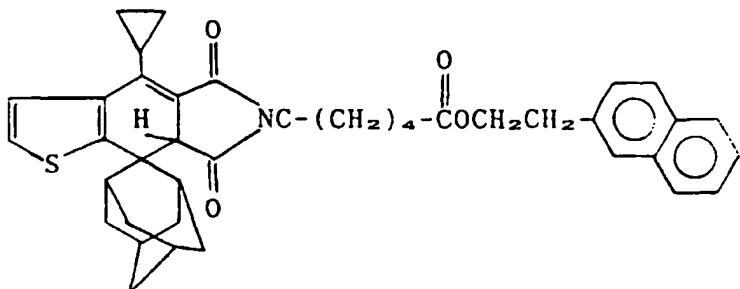
carbon of the cyclopropyl group near δ 9.7 ppm, a peak based on the carbons of the thiophene group and the carbons of the naphthalene ring near δ 110-160 ppm, and a peak based on the carbon of the $>\text{C=O}$ bond near δ 160-170 ppm.

[0131] From the above results, the isolated products was determined to be a fulgimide compound of the following structural formula

5

10

15



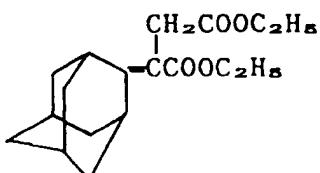
EXAMPLE 7

20

[0132] 11.3 g (0.049 mole) of cyclopropyl-(5-bromo-3-thienyl)ketone and 19.6 g (0.084 mole) of diethyladamantylidene succinate of the following formula

25

30

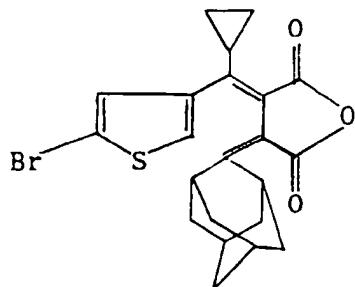


were dissolved in 200 cc of toluene to form a solution. The toluene solution was added dropwise over 3 hours in an atmosphere of nitrogen to a solution of 5 g of sodium hydride in 200 cc of toluene so that the temperature of the toluene solution became 0°C or below. After the addition, the mixture was vigorously stirred for 10 hours while the liquid temperature was maintained at 0°C or below. The mixture was hydrolyzed with an excessive amount of a 10 % alcoholic aqueous solution of potassium hydroxide and acidified with hydrochloric acid. The resulting dicarboxylic acid was treated with 100 cc of acetyl chloride, and purified by chromatography on silica gel to give 12.8 g of fulgide compound of the following formula

40

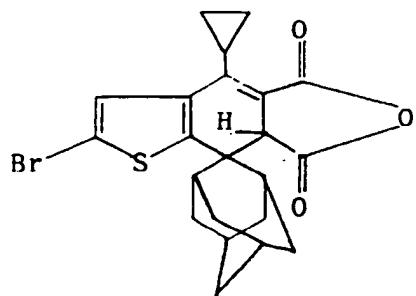
45

50



[0133] The resulting compound was refluxed in o-dichlorobenzene for 8 hours to rearrange it to a fulgide compound of the following formula

55



[0134] This compound was purified by chromatography on silica gel using benzene and ether as an eluent. By recrystallization from chloroform and hexane, it was obtained as yellow needles in a yield of 35 %. The elemental analysis values of this compound were C 59.35 %, H 4.79 %, O 10.81 %, S 7.25 % and Br 18.01 %, which well agreed with the calculated values for $C_{19}H_{19}O_3SBr$ (C 59.33 %, H 4.75 %, O 10.78 %, S 7.20 % and Br 17.94 %).

[0135] The proton NMR spectrum of the resulting compound was measured. The spectrum showed a peak of 1H based on the proton of the thiophene ring near δ 7.2 ppm, a peak of 1H based on the 1-5 shifted proton near δ 4.0 ppm, and a broad peak of 19H based on the protons of the cyclopropyl group and the adamantlylidene group near δ 1.2-2.5 ppm.

[0136] The ^{13}C -NMR spectrum of the resulting compound was also measured. It showed a peak based on the carbons of the bicyclo[3.3.1]9-nonylidene group near δ 27-52 ppm, a peak based on the carbon of the cyclopropyl group near δ 9.7 ppm, a peak based on the carbons of the thiophene ring near δ 110-160 ppm, and a peak based on the carbon of the $>C=O$ bond near δ 160-170 ppm.

[0137] From the above results, the isolated products was identified as a compound of the above structural formula.

EXAMPLE 8

[0138] In the same way as in Examples 1 to 7, various compounds were synthesized from the starting materials shown in Tables 1 to 18. The yields of the products are also shown in Tables 1 to 18.

[0139] By the same elemental analysis, proton NMR spectrum analysis and ^{13}C -NMR spectral analysis as in Examples 1 to 7, the resulting compounds were determined to have the structures shown in Tables 1 to 18.

[0140] The results of the elemental analysis are shown in Tables 19 to 21.

35

40

45

50

55

Table 1

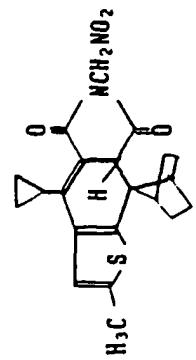
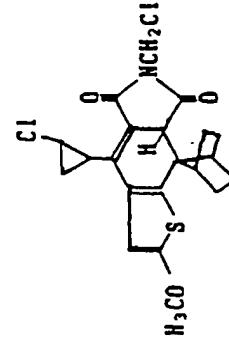
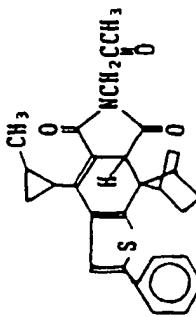
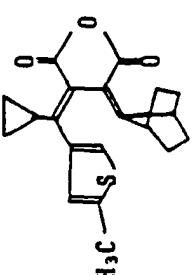
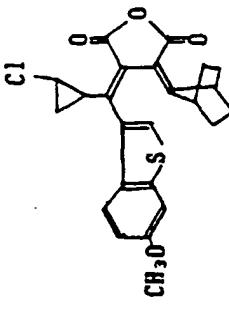
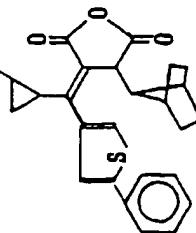
Starting Material	Product	Yield
	 <p>$\text{H}_2\text{NCH}_2\text{NO}_2$</p>	20
	 <p>Cl $\text{H}_2\text{NCH}_2\text{Cl}$</p>	15
	 <p>CH_3 $\text{H}_2\text{NCH}_2\text{CCH}_3$</p>	20
8	 <p>$\text{H}_2\text{NCH}_2\text{NO}_2$</p>	20
9	 <p>Cl CH_3O</p>	15
10	 <p>CH_3 $\text{H}_2\text{NCH}_2\text{CCH}_3$</p>	20

Table 2

Table 3

Starting Material	Product	Yield
14	 $\text{H}_2\text{NCH}_2\text{OCH}_2\text{CN}$	23
15	 $\text{H}_2\text{NCH}_2\text{CH}_2\text{CCH}_2\text{CH}_2\text{CNCH}_3$	15
16	 $\text{H}_2\text{NCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$	20

Table 4

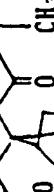
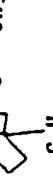
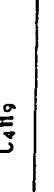
Yield	Product	
Starting Material		
23		
21		
20		
17		
18		
19		

Table 5

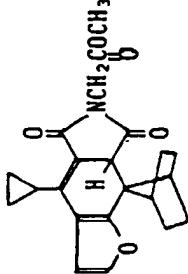
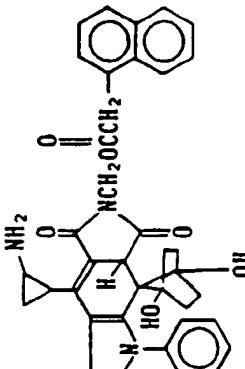
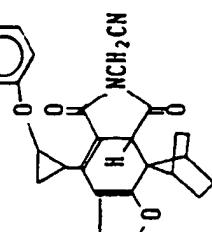
Starting Material	Product	Yield
20	 <chem>BrCH2C(=O)NCC(=O)c1c2c(c3c1C(=O)c4c3C4)C(=O)c5c4c(c6c5C(=O)c7c6C7)C(=O)c8c7c(c9c8C(=O)c1c9C1)C9</chem>	30
21	 <chem>BrCH2C(=O)NCC(=O)c1c2c(c3c1C(=O)c4c3C4)C(=O)c5c4c(c6c5C(=O)c7c6C7)C(=O)c8c7c(c9c8C(=O)c1c9C1)C9</chem>	50
22	 <chem>BrCH2CN</chem>	12

Table 6

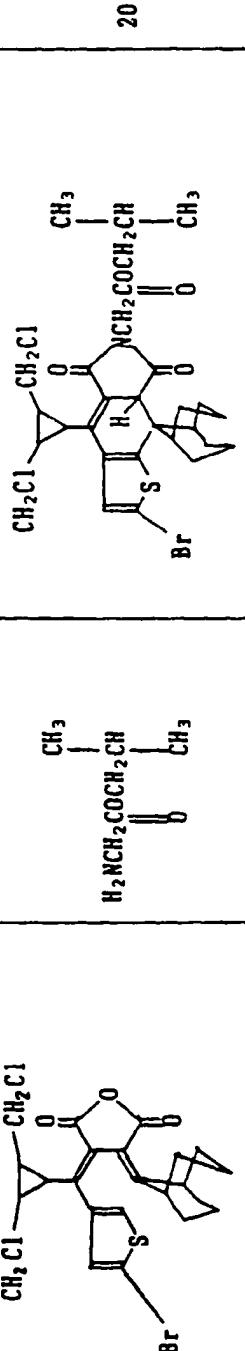
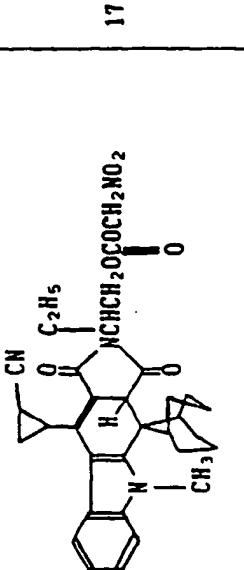
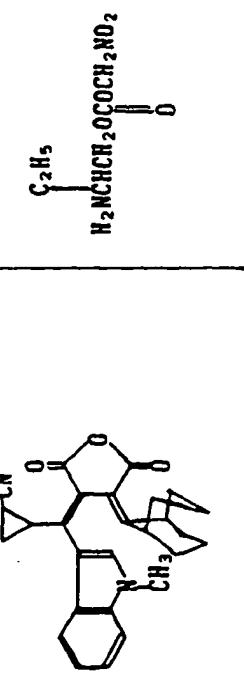
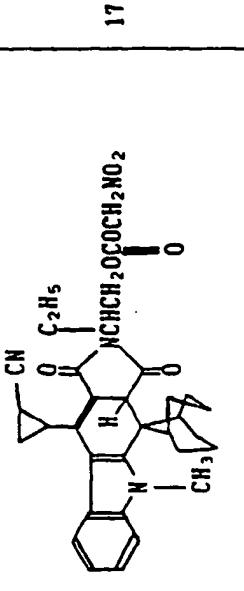
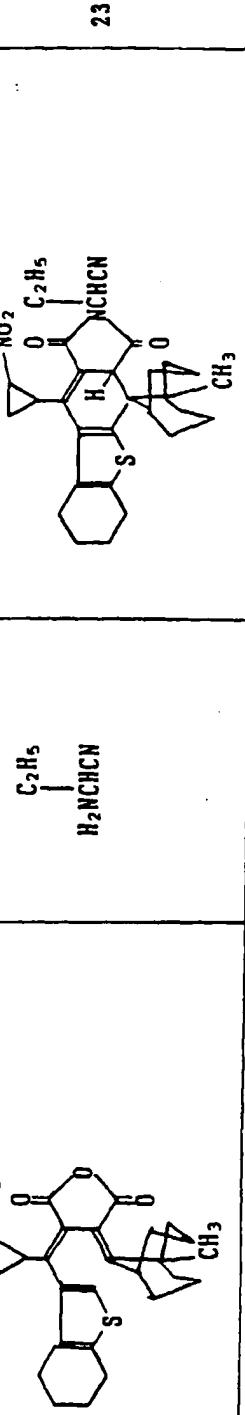
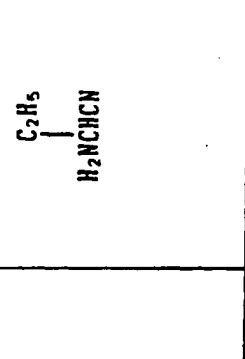
Starting Material	Product	Yield
23		 20
24		 17
25		 23

Table 7

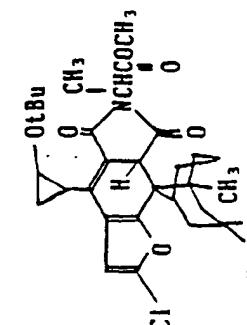
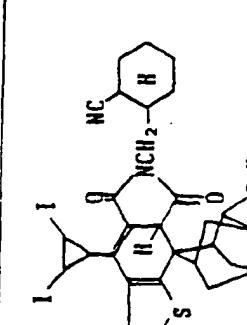
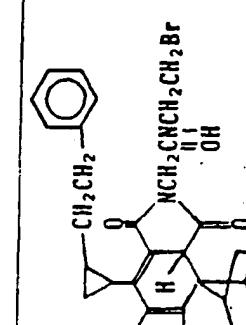
Starting Material	Product	Yield
26	 $\text{CH}_3\text{CH}_2\text{NHCOCOCH}_3$	20
27	 $\text{H}_2\text{NCH}_2\text{C}_2\text{H}_5$	19
28	 $\text{H}_2\text{NCH}_2\text{C}_2\text{H}_5$	25

Table 8

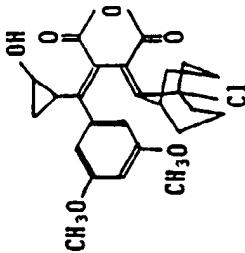
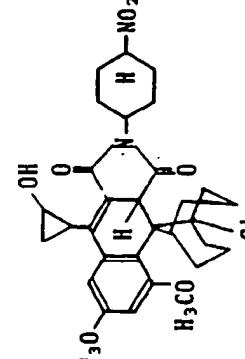
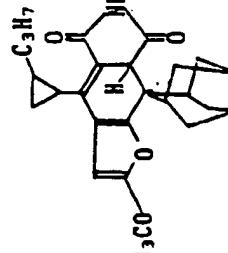
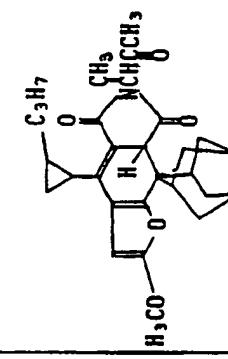
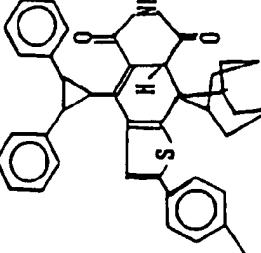
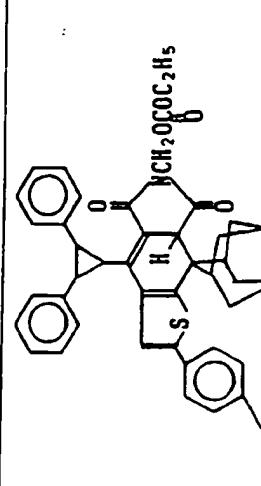
	Starting Material	Product	Yield
29			25
30			27
31			31

Table 9

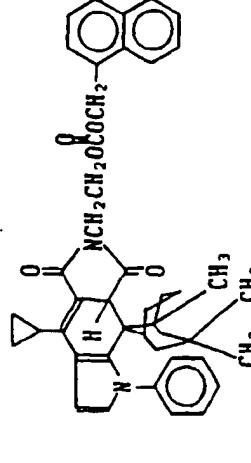
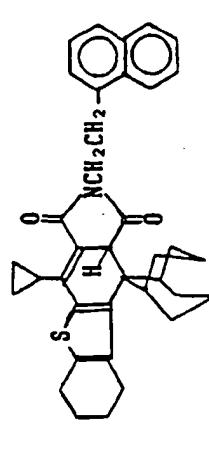
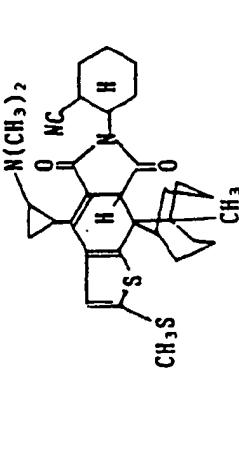
Starting Material	Product	Yield
32		50
33		45
34		37

Table 10

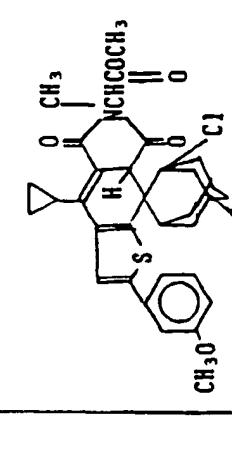
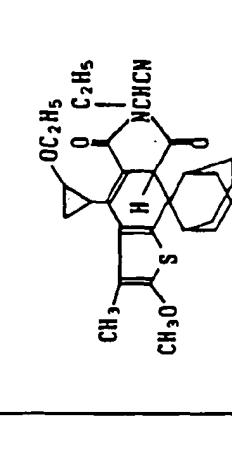
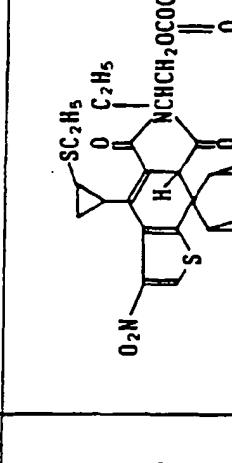
Starting Material	Product	Yield
35		18
36		25
37		20

Table 11

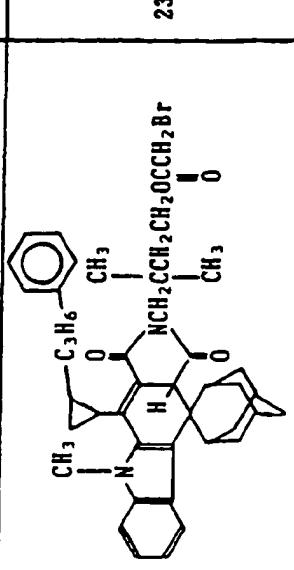
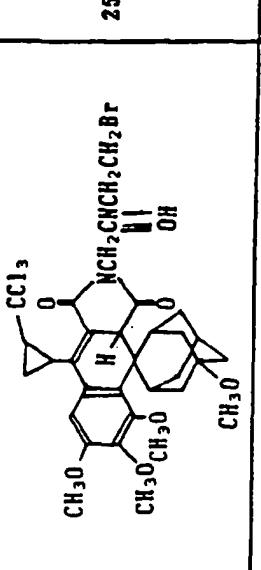
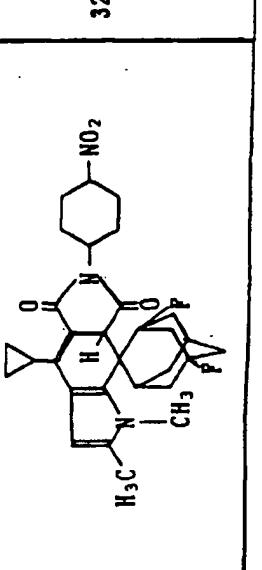
Starting Material	Product	Yield
38	 $\text{H}_2\text{NCH}_2\text{CCH}_2\text{CH}_2\text{OCCBr}$	23
39	 $\text{H}_2\text{NCH}_2\text{CNCBr}$	25
40	 $\text{H}_2\text{NCH}_2\text{NO}_2$	32

Table 12

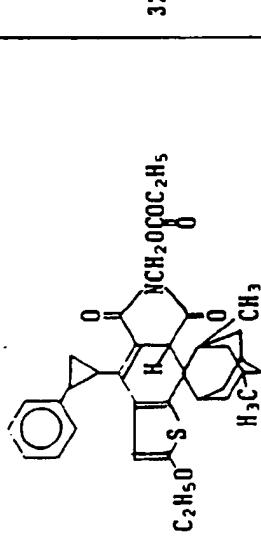
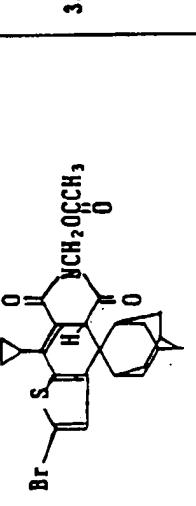
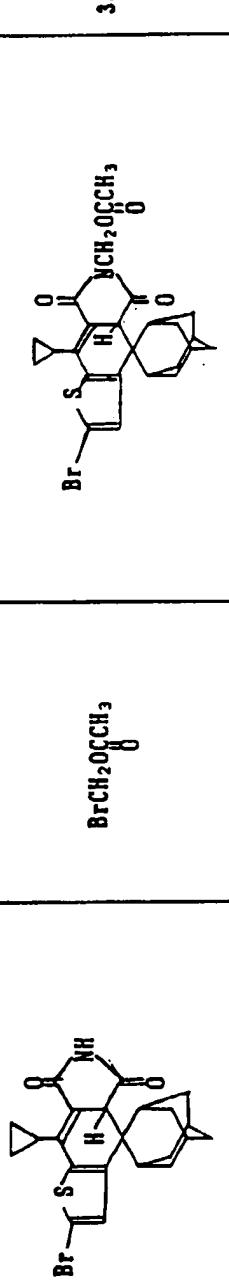
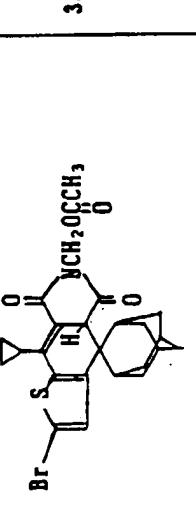
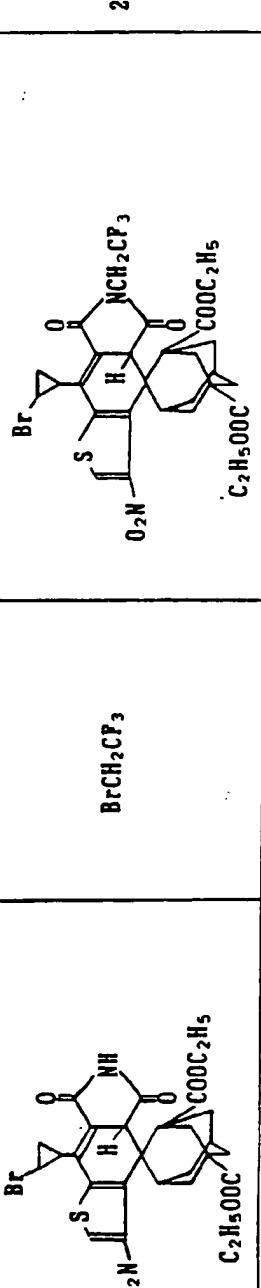
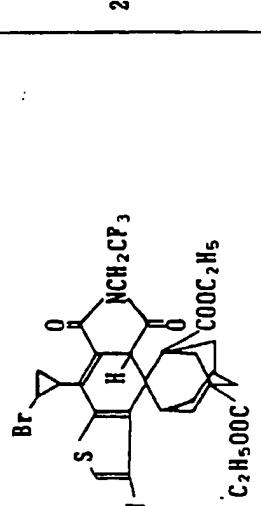
	Starting Material	Product	Yield
41	 <chem>CC1(C)CC2(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C1)C(=O)C(=O)N(C2)C(C)C</chem>	 <chem>CC1(C)CC2(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C1)C(=O)C(=O)N(C2)C(C)C</chem>	32
42	 <chem>CC1(C)CC2(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C(C)C1)C(=O)C(=O)N(C2)C(C)C</chem>	 <chem>CC1(C)CC2(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C(C)C1)C(=O)C(=O)N(C2)C(C)C</chem>	35
43	 <chem>CC1(C)CC2(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C(C)C1)C(=O)C(=O)N(C2)C(C)C</chem>	 <chem>CC1(C)CC2(C1)C(=O)C(=O)N(C2)C(C)C</chem> <chem>CC(C)C(C)C1C2C(C(C)C1)C(=O)C(=O)N(C2)C(C)C</chem>	27

Table 13

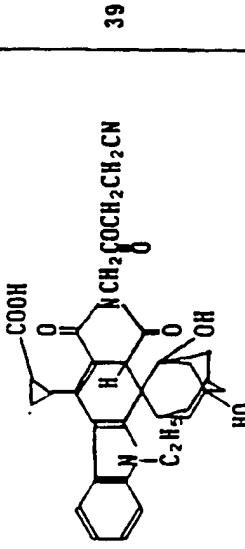
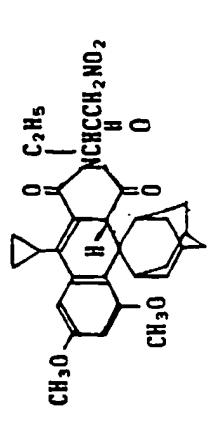
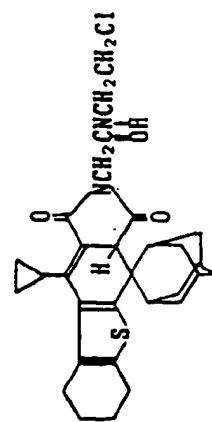
Starting Material	Product	Yield
44	 <chem>BrCH2COCH2CH2CN</chem>	39
45	 <chem>C2H5BrCH2CH2NO2</chem>	45
46	 <chem>BrCH2CNC(=O)CH2CH2Cl</chem>	30

Table 14

Starting Material	Product	Yield
		5
		10
		15
		20
		25
		30
		35
		40
		45
		50
		55
47	48	49

Table 15

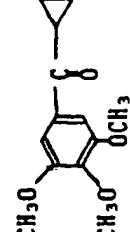
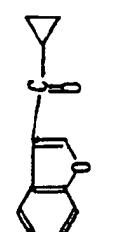
Starting Material	Product	Yield
50	 $\text{CH}_2-\text{C}(=\text{O})\text{C}_2\text{H}_5$ COOC_2H_5	33
51	 $\text{CH}_2-\text{C}(=\text{O})\text{C}_2\text{H}_5$ COOC_2H_5	35
52	 $\text{CH}_2-\text{C}(=\text{O})\text{C}_2\text{H}_5$ COOC_2H_5	17

Table 16

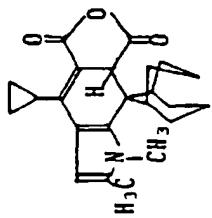
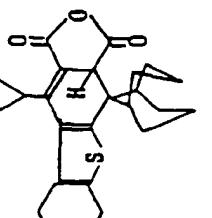
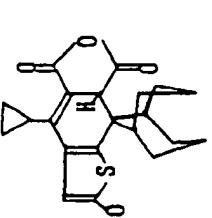
Starting Material	Product	Yield
53	 CCOOC_2H_5 $\text{CH}_2\text{COOC}_2\text{H}_5$	7
54	 CCOOC_2H_5 $\text{CH}_2\text{COOC}_2\text{H}_5$	12
55	 $\text{C}_2\text{H}_5\text{O}$	25

Table 17

Starting Material	Product	Yield	5	
			10	
56		15		
57		12		
58		25		

5

10

15

20

25

30

35

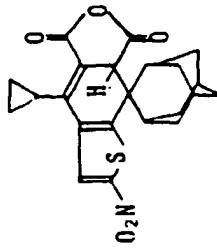
40

45

50

55

Table 18

Starting Material	Product	Yield
		27
		
59		

5 10 15 20 25 30 35 40 45 50 55

Table 19

No.	Elemental analysis value (%)						Calculated value			' ¹ H-NMR spectrum (ppm)			
	C	H	N	O	S	Others	C	H	N	O	S	Others	
8	63.37	5.61	7.06	16.11	8.11	63.3	5.56	7.03	16.06	8.05		δ 7.2:1H, δ 3.0~5.0:3H, δ 1.2~2.7:18H	
9	61.31	4.81	2.91	9.82	6.51	C1 14.9	61.23	4.73	2.86	9.79	6.54	C1 14.87	δ 7.0~8.0:3H, δ 3.0~5.0:6H, δ 1.2~2.7:15H
10	73.91	6.25	3.01	10.22	6.85	73.86	6.2	2.97	10.18	6.8			δ 7.0~8.0:6H, δ 3.0~5.0:6H, δ 1.2~2.7:17H
11	54.25	4.41	8.21	15.65	6.32	F 11.21	54.22	4.35	8.25	15.7	6.29	F 11.19	δ 7.3:1H, δ 3.0~5.0:7H, δ 1.2~2.7:14H
12	65.45	6.17	3.11	17.45		C1 7.91	65.43	6.15	3.05	17.43		C1 7.94	δ 7.0~8.0:2H, δ 3.0~5.0:5H, δ 1.2~2.7:2H
13	54.91	4.65	4.03	13.73		Br 22.85	54.8	4.74	3.99	13.69		Br 22.78	δ 7.0~8.0:4H, δ 3.0~5.0:6H, δ 1.2~2.7:23H
14	62.15	4.51	5.19	8.91	5.95	C1 13.51	62.11	4.47	5.17	8.86	5.92	C1 13.46	δ 7.0~8.0:7H, δ 3.0~5.0:5H, δ 1.2~2.7:12H
15	65.53	7.15	8.05	12.19	6.17	66.51	7.12	8.02	12.22	6.12			δ 7.0~8.0:2H, δ 3.0~5.0:7H, δ 1.2~2.7:28H
16	56.57	3.82	2.49	13.9		F 23.21	56.55	3.87	2.44	13.95		F 2.19	δ 7.0~8.0:4H, δ 3.0~5.0:10H, δ 1.2~2.7:8H
17	75.29	8.25	4.95	11.4		75.24	8.3	5.01	11.45				δ 7.0~8.0:2H, δ 3.0~5.0:7H, δ 1.2~2.7:3H
18	79.3	7.15	2.45	11.08		79.27	7.18	2.43	11.12				δ 7.0~8.0:9H, δ 3.0~5.0:9H, δ 1.2~2.7:23H
19	77.11	5.81	2.63	8.89	5.92	77.04	5.73	2.57	8.8	5.88			δ 7.0~8.0:1H, δ 3.0~5.0:6H, δ 1.2~2.7:14H
20	69.25	6.12	3.70	20.95		69.28	6.08	3.67	20.97				δ 7.0~8.0:2H, δ 3.0~5.0:6H, δ 1.2~2.7:15H
21	72.53	5.65	6.62	15.19		72.48	5.6	6.67	15.24				δ 7.0~8.0:14H, δ 3.0~5.0:7H, δ 1.2~2.7:14H
22	73.65	5.52	6.31	14.58		73.62	5.49	6.36	14.53				δ 7.0~8.0:7H, δ 3.0~5.0:3H, δ 1.2~2.7:24H
23	53.91	5.33	2.19	9.95	4.92	C1 11.32	53.96	5.31	2.17	9.92	4.97	C1 11.3	δ 7.2:1H, δ 3.0~5.0:9H, δ 1.2~2.7:24H
24	66.02	6.12	9.37	18.71		Br 12.39						Br 12.38	
25	67.55	6.59	7.91	12.04	6.05	65.99	6.04	9.33	18.65				δ 7.0~8.0:4H, δ 3.0~5.0:9H, δ 1.2~2.7:23H
26	67.11	7.34	2.49	16.71		67.52	6.61	7.87	11.99	6.01			δ 3.0~5.0:2H, δ 1.2~2.7:33H
27	52.45	5.65	3.45	3.91	3.93	C1 6.41	67.06	7.39	2.44	16.75		C1 6.36	δ 7.2:1H, δ 3.0~5.0:5H, δ 1.2~2.7:36H
28	59.45	5.51	4.13	9.33	4.71	C1 5.35	52.43	5.62	3.4	3.88	3.89	C1 30.78	δ 3.0~5.0:3H, δ 1.2~2.7:43H
29	63.55	6.37	4.81	19.13		Br 11.65	59.43	5.57	4.08	9.31	4.67	C1 5.31	δ 7.0~8.0:6H, δ 3.0~5.0:7H, δ 1.2~2.7:25H
30	72.65	7.79	2.95	16.72		C1 6.25	63.53	6.36	4.78	19.11		C1 11.63	
31	74.05	6.11	1.99	13.47	4.51	72.62	7.78	2.92	16.68			C1 6.22	δ 7.0~8.0:2H, δ 3.0~5.0:8H, δ 1.2~2.7:27H
32	77.41	6.85	4.15	11.67		74.03	6.07	1.96	13.45	4.49			δ 7.2:1H, δ 3.0~5.0:5H, δ 1.2~2.7:31H
						77.39	6.79	4.1	11.72				δ 7.0~8.0:15H, δ 3.0~5.0:8H, δ 1.2~2.7:20H
													δ 7.0~8.0:14H, δ 3.0~5.0:7H, δ 1.2~2.7:25H

5 10 15 20 25 30 35 40 45 50 55

Table 20

No.	Elemental analysis value (%)								Calculated value				'H-NMR spectrum (ppm)	
	C	H	N	O	S	Others	C	H	N	O	S	Others		
33	79.14	7.09	2.53	5.72	5.73	79.11	7	2.49	5.7	5.71			δ7.0~8.0:7H, δ3.0~5.0:3H, δ1.2~2.7:2H	
34	68.21	7.35	7.51	5.72	11.32	68.17	7.33	7.45	5.68	11.37			δ7.2:1H, δ3.7:1H, δ1.2~2.7:3H	
35	63.11	5.31	2.27	12.75	5.13	C1	11.63	63.06	5.29	2.23	12.73	5.1	C1 11.6	
36	69.25	7.03	5.43	12.34	6.23		69.2	6.97	5.38	12.29	6.16		δ7.0~8.0:5H, δ3.0~5.0:8H, δ1.2~2.7:2H	
37	56.47	5.73	6.39	21.87	9.81		56.43	5.65	6.37	21.83	9.72		δ3.0~5.0:7H, δ1.2~2.7:2H	
38	71.2	6.92	3.65	8.47		Br	10.65	70.3	6.84	3.73	8.51	Br	10.63	δ7.0~8.0:9H, δ3.0~5.0:6H, δ1.2~2.7:3H
39	51.92	4.97	3.72	14.73		C1	14.35	51.88	5.01	3.67	14.66	C1	14.32	δ7.0:1H, δ3.0~5.0:16H, δ1.2~2.7:2H
40	66.82	6.57	7.83	11.89		P	7.12	66.77	6.54	7.79	11.86	F	7.04	δ7.2:1H, δ3.0~5.0:4H, δ1.2~2.7:3H
41	70.25	6.73	2.31	15.63	5.27		70.22	6.71	2.27	15.59	5.21		δ7.0~8.0:6H, δ3.0~5.0:7H, δ1.2~2.7:2H	
42	58.17	5.11	2.73	12.36	6.25	Br	15.42	58.14	5.07	2.71	12.39	Br	15.47	δ7.2:1H, δ3.0~5.0:3H, δ1.2~2.7:2H
43	50.39	4.21	3.99	17.85	4.53	F	8.02	50.36	4.23	3.92	17.89	F	7.97	δ7.2:1H, δ3.0~5.0:7H, δ1.2~2.7:2H
44	66.57	5.82	6.91	20.82		Br	11.21					Br	11.17	
45	67.82	6.57	5.13	20.45			66.55	5.75	6.85	20.86			δ7.0~8.0:5H, δ3.0~5.0:9H, δ1.2~2.7:2H	
46	66.73	6.55	5.17	8.91	5.92	C1	6.81	66.71	6.53	5.19	8.89	C1	6.75	δ7.0~8.0:2H, δ3.0~5.0:8H, δ1.2~2.7:2H
47	71.52	6.37	6.71	10.33	5.12		71.47	6.32	6.76	10.29	5.16		δ3.0~5.0:4H, δ1.2~2.7:3H	
48	80.11	7.75	2.27	5.12	5.15		80.09	7.52	2.22	5.08	5.09		δ7.0~8.0:7H, δ3.0~5.0:3H, δ1.2~2.7:2H	
49	73.41	5.37	12.82	8.55			73.38	5.35		12.75	8.52		δ7.0~8.0:4H, δ3.7:1H, δ1.2~2.7:15H	
50	50.82	3.43	10.17	6.79		F	12.07	50.75	3.41	10.14	6.77	F	12.04	δ7.2:1H, δ3.7:1H, δ1.2~2.7:14H
51	70.25	6.42		23.41			70.23	6.38		23.39			Br 16.88	
52	76.71	5.62		17.83			76.65	5.59		17.76			δ7.0:1H, δ3.0~5.0:10H, δ1.2~2.7:15H	
53	75.63	7.47		3.85	13.15		75.59	7.45	3.83	13.13			δ7.0~8.0:4H, δ3.7:1H, δ1.2~2.7:15H	
54	73.45	6.87		11.7	7.81		73.5	6.91		11.75	7.85		δ7.2:1H, δ3.0~5.0:4H, δ1.2~2.7:2H	
55	69.35	6.61		16.11	8.02		69.32	6.58		16.06	8.04		δ3.7:1H, δ3.0~5.0:3H, δ1.2~2.7:2H	

5

10

15

20

25

30

35

40

45

50

55

Table 21

No.	Elemental analysis value (%)						Calculated value						^1H -NMR spectrum (ppm)					
	C	H	N	O	S	Others	C	H	N	O	S	Others	C	H	N	O	S	Others
56	59.91	5.51	10.5	6.92	Br	17.35	59.87	5.46	10.4	6.95	Br	17.32	δ7.2:1H, δ3.7:1H, δ1.2~2.7:23H					
57	78.92	7.12	3.22	10.92			78.88	7.08	3.17	10.87			δ7.0~8.0:4H, δ3.0~5.0:3H, δ1.2~2.7:24H					
58	61.3	4.93	10.65	C1	16.17	61.2	4.91		10.63		C1	16.15	δ7.2:1H, δ3.7:1H, δ1.2~2.7:20H					
59	66.53	5.35		20.15	8.02		66.48	5.33		20.33	8.07		δ7.2:1H, δ3.7:1H, δ1.2~2.7:19H					

EXAMPLE 9

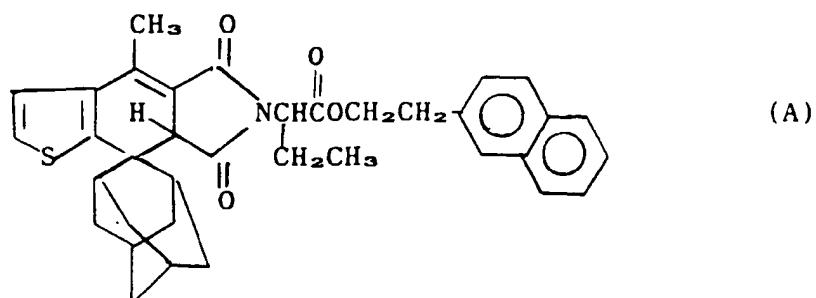
[0141] In each run, 0.3 part by weight of each the compounds represented by structural formulae (1) to (59) produced in Examples 1 to 8, 10 parts by weight of poly(methyl methacrylate) and 100 parts by weight of benzene were dispersed, and the resulting mixture was cast into a film on a slide glass (11.2 x 3.7 cm). The thickness of the cast film was adjusted to 0.1 mm.

5 Xenon light was irradiated onto the resulting photochromic film by using a xenon long-life fadeometer (FAL-25AX-HC; output 2.5 KW; light source xenon long-life arc lamp) made by Suga Testing Instrument Co., Ltd. The initial coloration density (absorbance), maximum absorption wavelength (λ_{\max}) and fatigue life ($T_{1/2}$) in accordance with JIS L 0843 and JIS B 7754 of the photochromic film were measured.

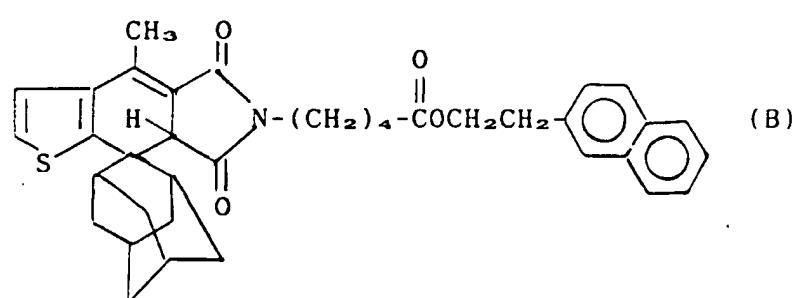
10 [0142] $T_{1/2}$ is defined as the time required for the color density to decrease to half of its initial value when the film is exposed to the fadeometer.

[0143] The results of measurements are shown in Tables 22 and 23. For comparison, the following (A) to (H) were also tested in the same way as above, and the fatigue life of the resulting photochromic films were measured.

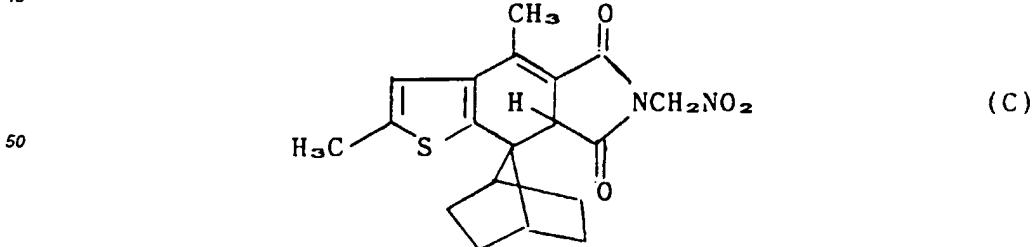
15



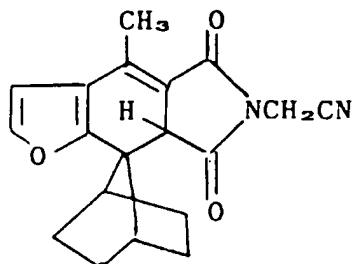
30



45



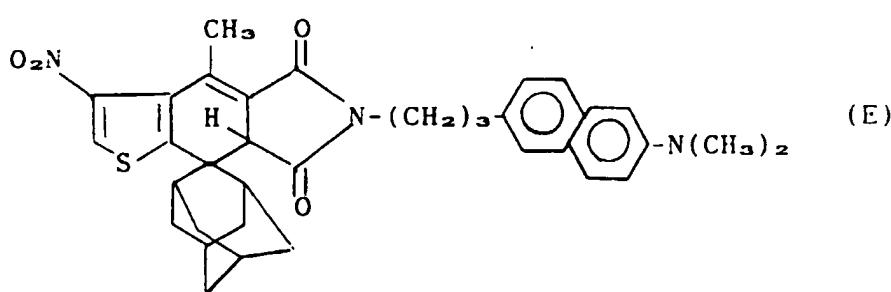
5



(D)

10

15



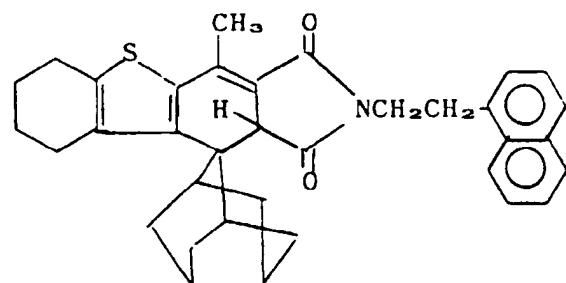
(E)

20

30

35

40

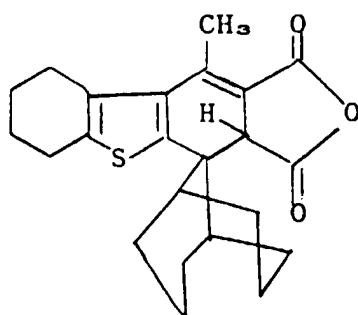


(F)

45

50

55



(G)

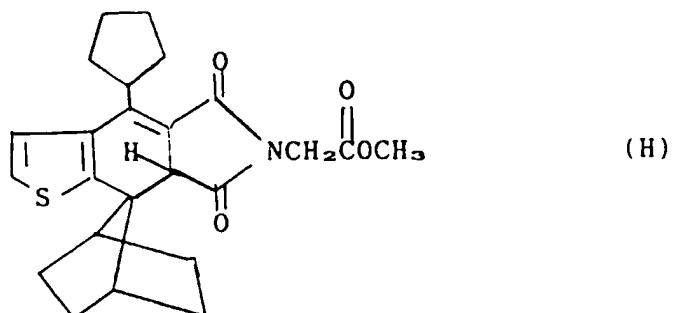


Table 22

No.	Fulgitimide or fulgide compound	Initial color density (%)	T _{1/2} (hours)	λ _{max} (nm)
1	(1)	0.85	77	549
2	(2)	0.78	89	563
3	(3)	0.88	45	545
4	(4)	0.85	52	542
5	(5)	0.69	61	532
6	(6)	0.72	57	549
7	(7)	1.21	54	529
8	(8)	0.69	75	571
9	(9)	0.73	51	548
10	(10)	0.83	80	610
11	(11)	0.75	65	530
12	(12)	0.78	77	581
13	(13)	0.69	47	495
14	(14)	0.58	69	552
15	(15)	0.69	65	613
16	(16)	0.82	91	498
17	(17)	0.58	58	568
18	(18)	0.62	61	603
19	(19)	0.58	81	524
20	(20)	0.82	89	531
21	(21)	0.78	71	613
22	(22)	0.81	88	554
23	(23)	0.87	53	539
24	(24)	0.67	64	576
25	(25)	0.71	76	562
26	(26)	0.78	72	546
27	(27)	0.68	51	553
28	(28)	0.56	54	526
29	(29)	0.52	62	588
30	(30)	0.73	78	569

Table 23

	No.	Fulgimide or fulgide compound	Initial color density (%)	T _{1/2} (hours)	λ _{max} (nm)
5	31	(31)	0.77	81	624
	32	(32)	0.72	68	577
	33	(33)	0.56	78	519
	34	(34)	0.88	49	625
	35	(35)	0.73	85	574
	36	(36)	0.86	88	576
	37	(37)	0.77	75	540
	38	(38)	0.61	68	592
10	39	(39)	0.58	65	527
	40	(40)	0.77	71	532
	41	(41)	0.82	65	557
	42	(42)	0.57	68	548
	43	(43)	0.62	72	509
	44	(44)	0.75	62	576
15	45	(45)	0.54	65	579
	46	(46)	0.71	59	563
	47	(47)	0.72	52	529
	48	(48)	0.75	62	588
	49	(49)	1.15	58	564
	50	(50)	0.90	48	518
20	51	(51)	0.92	52	561
	52	(52)	1.21	54	534
	53	(53)	1.18	56	525
	54	(54)	1.09	52	568
	55	(55)	1.25	58	545
	56	(56)	1.33	49	530
25	57	(57)	1.21	55	559
	58	(58)	1.24	48	554
	59	(59)	1.21	57	524
	Comp. 1	(A)	0.51	24	520
	▪ 2	(B)	0.49	16	538
	▪ 3	(C)	0.72	30	556
30	▪ 4	(D)	0.90	48	535
	▪ 5	(E)	0.32	14	535
	▪ 6	(F)	0.47	13	508
	▪ 7	(G)	0.71	10	585
	▪ 8	(H)	0.80	32	540

EXAMPLE 10

[0144] 0.1 g of each of the fulgimide or fulgide compounds produced in Examples 1 to 8 was dissolved in 100 cc of silicone oil. The solution was impregnated in the surface of a lens composed of poly(allyl diglycol carbonate) at 200°C for 1 hour. The concentration of the solution was adjusted to 1.0×10^{-4} mole/g. The durability of the film was measured as in Example 9. The results are shown in Table 24.

Table 24

	No.	Fulgimide or fulgide compound	Initial color density (%)	T _{1/2} (hours)	λ _{max} (nm)
55	1	(1)	0.78	82	554
	2	(2)	0.71	91	568

Table 24 (continued)

No.	Fulgimide or fulgide compound	Initial color density (%)	T _{1/2} (hours)	λ _{max} (nm)
5	3 (3)	0.81	49	550
	4 (8)	0.63	80	578
	5 (10)	0.82	85	615
	6 (20)	0.73	95	535
	7 (22)	0.70	93	559
	8 (25)	0.65	79	565
10	9 (30)	0.68	85	571
	10 (31)	0.69	86	616
	11 (33)	0.49	80	525
	12 (35)	0.67	90	580
	13 (36)	0.77	95	582
	14 (40)	0.70	74	535
15	15 (42)	0.51	71	553
	16 (48)	0.67	65	590
	17 (51)	0.82	55	562
	18 (53)	1.08	60	530
	19 (54)	0.99	54	573
	20 (55)	1.13	61	550

25 EXAMPLE 11

[0145] One hundred parts by weight of benzene, 10 parts by weight of poly(methyl methacrylate), 0.2 part by weight of the fulgimide compound obtained in Example 1 and 0.2 part by weight of each of the compounds shown in Table 25 as an ultraviolet stabilizer were mixed to form a solution. The solution was cast on a slide glass (11.2 x 3.7 cm) to form a cast film having a thickness of 0.1 mm.

[0146] The fatigue life of photochromic film was measured as in Example 9 by a xenon long-life fadeometer (FAL-25AX-HC made by Suga Testing Instrument Co., Ltd.). The results are shown in Table 25.

Table 25

No.	Ultraviolet stabilizer	T _{1/2} (hours)
35	1 Cyasorb UV1084	310
	2 Irgastab 2002	299
	3 Rylex NBC	323
	4 UV Chek AM101	295
	5 UV Chek AM105	272
	6 Tinuvin 765	325
	7 Chimassorb 944	283
	8 Cyasorb 3346	336
	9 Tinuvin 622	327
	10 Spinuvex A-36	302
	11 Tinuvin 144	310

50

EXAMPLE 12

[0147] Example 11 was repeated except that the fulgimide compound obtained in Example 2 was used instead of fulgimide compound used in Example 11. The results are shown in Table 26.

Table 26

No.	Ultraviolet stabilizer	T _{1/2} (hours)
1	Cyasorb UV1084	355
2	Irgastab 2002	340
3	Rylex NBC	369
4	UV Chek AM101	336
5	UV Chek AM105	308
6	Tinuvin 765	373
7	Chimassorb 944	325
8	Cyasorb 3346	385
9	Tinuvin 622	375
10	Spinuvex A-36	346
11	Tinuvin 144	355

5

10

15

EXAMPLE 13

[0148] Example 11 was repeated except that each of the ultraviolet stabilizers shown in Table 27 was used. The results are summarized in Table 27.

25

Table 27

Run	Ultraviolet stabilizer			T _{1/2} (hours)
	Type	Amount added	Proportion per 100 parts by weight of the fulgimide compound (parts by weight)	
1	Cyasorb UV1084	0.002	1	220
2	"	0.1	50	293
3	"	20	10000	367
4	"	0.8	400	330
5	Tinuvin 765	0.002	1	213
6	"	0.1	50	307
7	"	20	10000	375
8	"	0.8	400	340

EXAMPLE 14

45

[0149] Example 11 was repeated except that the fulgimide or fulgide compounds shown in Table 28 were used instead of the fulgimide compounds in Example 11, and Cyasorb UV1084 was used as the ultraviolet stabilizer. The results are shown in Table 28.

50

55

Table 28

No.	Fulgimide or fulgide compound	T _{1/2} (hours)
1	(2)	350
2	(4)	210
3	(5)	244
4	(6)	210
5	(7)	220
6	(12)	320

Table 28 (continued)

No.	Fulgimide or fulgide compound	T _{1/2} (hours)
5	7 (17)	230
	8 (40)	280
	9 (41)	263
	10 (45)	265
	11 (49)	235
10	12 (50)	200
	13 (56)	190
	14 (57)	220
	15 (59)	228

15

EXAMPLE 15

[0150] A fulgide or fulgimide compound (0.04 part) shown in Tables 29 and 30, 0.04 part of a chromene compound shown in Tables 29 and 30, 70 parts of tetraethylene glycol dimethacrylate, 15 parts of triethylene glycol dimethacrylate,

20 10 parts of glycidyl methacrylate, 5 parts of 2-hydroxyethyl methacrylate and 1 part of p-butyl ND as a polymerization catalyst were well mixed until they were completely dissolved. The mixed solution was injected into a mold which was made of a glass plate and a gasket formed of an ethylene-vinyl acetate copolymer, and was heated to a temperature of 35 to 90°C in an air oven over a period of 20 hours for polymerization. After the polymerization was over, the polymer was withdrawn from the glass plate of the mold.

25 [0151] The resulting polymerized plate was irradiated with sunlight for 10 minutes. On this occasion, a color tone of said plate was visually observed. In this polymerized plate, the fulgide or fulgimide compound and the chromene compound were measured for fatigue life in the same manner as in Example 9. Further, a-color tone of the polymerized plate was visually observed in T_{1/2} (hrs.) of the fulgide or fulgimide compound. The results are shown in Tables 29 and 30.

30

Table 29

No.	Fulgide or fulgimide No.	Chromene compound No.	T _{1/2} of fulgide or fulgimide compound (hrs.)	T _{1/2} of chromene compound (hrs.)	Color tone in T ₀	Color tone in T _{1/2} No.
35	1 2 (0.05)	2 (0.03)	210	210	brown	brown
	2 8 (0.05)	1 (0.03)	180	170	gray	gray
	3 10 (0.05)	3 (0.08)	190	150	green	bluish gray
	4 12 (0.05)	4 (0.08)	184	180	gray	gray
	5 15 (0.05)	5 (0.04)	160	192	green	light gray
40	6 17 (0.05)	5 (0.03)	146	120	gray	gray
	7 21 (0.05)	2 (0.03)	172	170	green	green
	8 24 (0.05)	4 (0.04)	158	152	gray	gray
	9 30 (0.05)	1 (0.03)	186	170	gray	gray
	10 36 (0.05)	2 (0.03)	206	190	gray	gray
45	11 44 (0.05)	3 (0.08)	154	160	gray	gray
	12 45 (0.05)	2 (0.03)	160	175	gray	light gray
	13 46 (0.05)	5 (0.07)	148	155	amber	amber
	14 48 (0.05)	1 (0.04)	154	148	gray	gray
	15 54 (0.05)	2 (0.03)	134	165	gray	brown

Note: Unit of parenthesized figures: parts by weight

55

Table 30

No.	Fulgide or fulgimide No.	Chromene compound No.	T _{1/2} of fulgide or fulgimide compound (hrs.)	T _{1/2} of chromene compound (hrs.)	Color tone in T ₀	Color tone in T _{1/2} No.
16	2 (0.05)	1/2 (0.02/0.02)	210	225	brown	brown
17	48 (0.05)	1/2 (0.015/0.015)	154	160	gray	gray
18	2/48 (0.025/0.025)	2 (0.04)	180	190	gray	gray
19	2/48 (0.025/0.025)	1 (0.04)	180	190	light gray	gray
20	2/48 (0.025/0.025)	1/2 (0.015/0.015)	180	165	gray	gray

EXAMPLE 16

[0152] A fulgide or fulgimide compound (0.2 part) shown in Table 31, 0.2 part of a chromene compound shown in Table 31, 0.7 part of an ultraviolet light stabilizer, 70 parts of tetraethylene glycol dimethacrylate, 15 parts of triethylene glycol dimethacrylate, 10 parts of glycidyl methacrylate, 5 parts of 2-hydroxyethyl methacrylate and 1 part of p-butyl ND as a polymerization catalyst were well mixed until they were completely dissolved. A polymerized plate was obtained from the resulting mixed solution in the same manner as in Example 15, and the fulgide or fulgimide compound and the chromene compound were measured for fatigue life. The results are shown in Table 31.

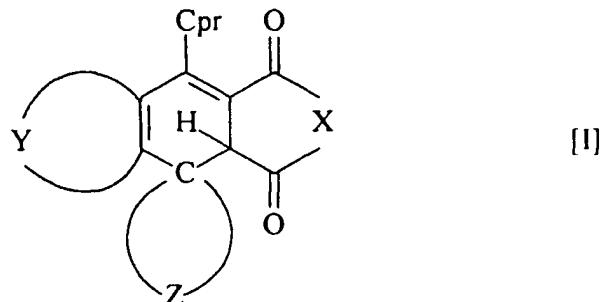
Table 31

No.	Fulgide or fulgimide No.	Chromene compound No.	UV stabilizer	T _{1/2} of fulgide or fulgimide compound (hrs.)	T _{1/2} of chromene compound (hrs.)
1	2 (0.05)	1 (0.03)	Irgastab 2002 (0.5)	450	480
2	2 (0.05)	2 (0.05)	LA-63 (0.5)	480	480
3	2 (0.05)	3 (0.01)	Cyasorb 944 (0.5)	400	400
4	2 (0.05)	4 (0.01)	LS-2626 (0.4)	490	480
5	2 (0.05)	5 (0.05)	Mark LA-87 (0.5)	440	450
6	48 (0.05)	1 (0.04)	Spinuvex A-36 (0.6)	430	430
7	48 (0.05)	2 (0.05)	Cyasorb UV1084 (0.6)	420	430
8	48 (0.05)	3 (0.1)	Tinuvin 765 (0.7)	450	420
9	48 (0.05)	4 (0.1)	UV Chek AM101 (0.4)	440	430
10	48 (0.05)	5 (0.05)	Tinuvin 622 (0.7)	450	430
11	2 (0.05)	2 (0.04)	UV Chek AM105 (0.7)	430	440
12	2 (0.05)	2 (0.04)	Tinuvin 765 (0.1)	350	340
13	2 (0.05)	2 (0.04)	Tinuvin 765 (0.2)	360	350
14	2 (0.05)	2 (0.04)	Tinuvin 765 (0.5)	390	400
15	2 (0.05)	2 (0.04)	Tinuvin 765 (1.0)	470	480
16	2 (0.05)	2 (0.04)	Tinuvin 765 (2.0)	490	500
17	2 (0.05)	2 (0.04)	Tinuvin 765 (10.0)	510	520

Claims

1. A compound of formula (I)

5



10

15

wherein

20



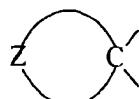
25

represents a divalent aromatic hydrocarbon group or a divalent unsaturated heterocyclic group each of which may optionally be substituted by a halogen atom, a nitro group, a cyano group, an amino group, alkylthio group having 1 to 4 carbon atoms, aryl group having 6 to 10 carbon atoms, alkyl group having 1 to 4 carbon atoms or alkoxy group having 1 to 4 carbon atoms;

Cpr represents a cyclopropyl group which may optionally be substituted by a halogen atom, nitro group, cyano group, amino group, alkylthio group having 1 to 4 carbon atoms, aryl group having 6 to 10 carbon atoms, alkyl group having 1 to 4 carbon atoms or alkoxy group having 1 to 4 carbon atoms.

30

35



40

represents a norbornylidene group, a bicyclo[3.3.1]nonylidene group, or an adamantlylidene group each of which may optionally be substituted by a halogen atom, a hydroxyl group, alkyl group having 1 to 4 carbon atoms alkoxy group having 1 to 4 carbon atoms, alkoxy carbonyl group having 2 to 10 carbon atoms, aralkyl group having 7 to 9 carbon atoms or aryl group having 6 to 10 carbon atoms; and X represents an oxygen atom, the group >N-R₁₁, the group >N-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂, the group >N-A₃-A₄, or the group >N-A₃-R₁₃.

in which

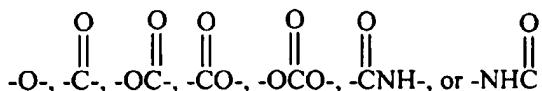
45

R₁₁ represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, or an aryl group having 6 to 10 carbon atoms,

A₁ and A₂ are identical or different and each represents an alkylene group having 1 to 10 carbon atoms, an alkylidene group having 2 to 10 carbon atoms, a cycloalkylene group having 3 to 10 carbon atoms or an alkylcycloalkanediyl group having 6 to 10 carbon atoms,

50

B₁ and B₂ are identical or different, and each represents



m and n, independently from each other, represents 0 or 1, provided that when m is 0, n is also 0,

R_{12} represents an alkyl group having 1 to 10 carbon atoms, a naphthyl group or a naphthylalkyl group having 1 to 4 carbon atoms in the alkyl moiety, the alkyl group having 1 to 10 carbon atoms being optionally substituted by 1 to 3 substituents which are each independently a halogen atom, cyano group or nitro group, and the naphthyl or naphthylalkyl group being optionally substituted by 1 to 3 substituents which are each independently a halogen atom, cyano group, nitro group, alkylamino group having 1 to 3 carbon atoms, alkyl group having 1 to 3 carbon atoms or alkoxy group having 1 to 3 carbon atoms,

A_3 represents an alkylene group having 1 to 10 carbon atoms, an alkylidene group having 2 to 10 carbon atoms, a cycloalkylene group having 3 to 10 carbon atoms, or an alkylcycloalkanediyl group having 6 to 10 carbon atoms.

A_4 represents a naphthyl group which may be substituted by 1 to 3 substituents which are each independently a halogen atom, cyano group, nitro group, alkylamino group having 1 to 3 carbon atoms, alkyl group having 1 to 3 carbon atoms or alkoxy group having 1 to 3 carbon atoms, and

R_{13} represents a halogen atom, a cyano group or a nitro group.

- 15 2. The compound of claim 1 in which X is the group >N-A₃-R₁₃.

3. The compound of claim 1 in which X is the group >N-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂.

20 4. The compound of claim 1 in which X is the group >N-A₃-A₄.

5. The compound of any one of claims 1 to 4 in which

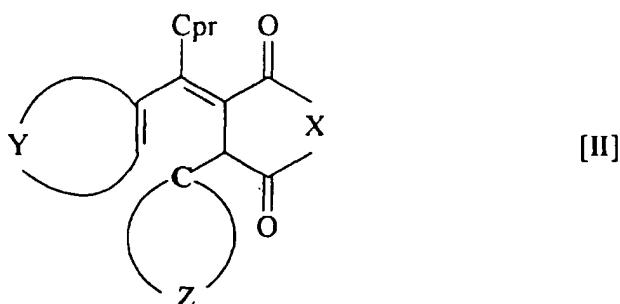
25



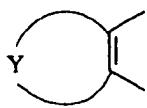
represents an aryl group having 6 to 14 carbon atoms, a 5- or 6-membered hetero-monocyclic group containing 1 to 3 nitrogen, oxygen or sulfur atoms, or a condensed heterocyclic group resulting from fusion of a benzene or cyclohexene ring to the heterocyclic group, each of which may be substituted by 1 to 3 substituents which are each independently a halogen atom, nitro group, cyano group, amino group, alkylthio group having 1 to 4 carbon atoms, aryl group having 6 to 10 carbon atoms, alkyl group having 1 to 4 carbon atoms or alkoxy group having 1 to 4 carbon atoms.

6. A process for producing a compound as claimed in any one of claims 1 to 5 which comprises cyclizing a compound of formula (II)

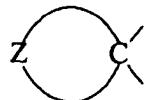
40



wherein

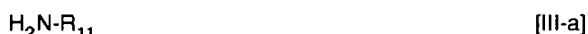


Cpr



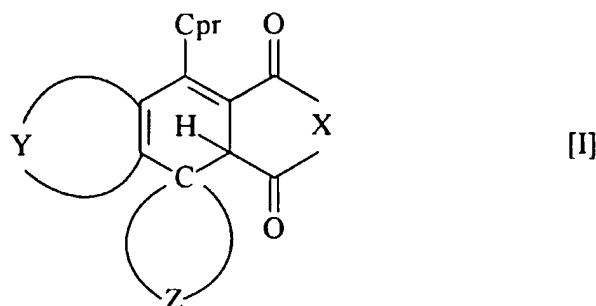
15 and X are as defined in claim 1,

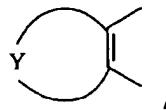
or reacting the compound of formula [II] in which X is an oxygen atom with an amine compound of formula [III-a], [III-b], [III-c] or [III-d]



wherein R_{11} , R_{12} , R_{13} , A_1 , A_2 , A_3 , A_4 , B_1 , B_2 , m and n are as defined in claim 1,
and then cyclizing the reaction product.

35 7. A process for producing a compound of formula [I]

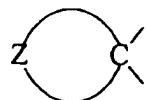




5

Cpr

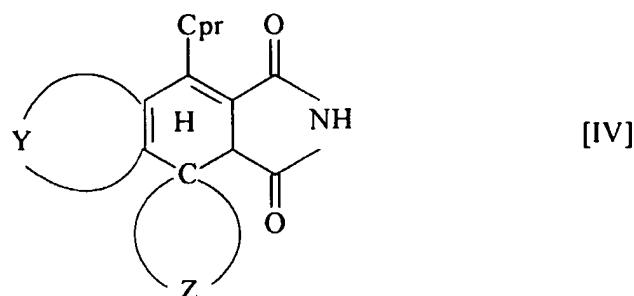
10



15

and X are as defined in claim 1, provided that X is not an oxygen atom which comprises reacting an imide compound of formula [IV]

20

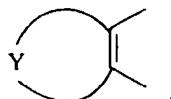


25

30

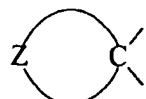
wherein

35



40

Cpr, and



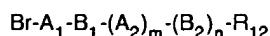
45

are as defined in claim 1 with an alkali metal, and then reacting the product with a bromine compound of formula [V-a], [V-b], [V-c] or [V-d]

50

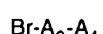


[V-a]



[V-b]

55



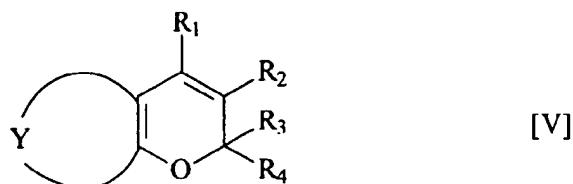
[V-c]

Br-A₃-R₁₃

[V-d]

5 wherein R₁₁, R₁₂, R₁₃, A₁, A₂, A₃, A₄, B₁, B₂, m and n are as defined in claim 1.

8. A composition comprising a high-molecular weight polymer and a compound as claimed in any one of claims 1 to 5.
9. The composition of claim 8 which further comprises an ultraviolet stabilizer.
10. The composition of claim 9 in which the ultraviolet stabilizer is a light extinguisher for oxygen in the singlet state or a hindered amine light stabilizer.
11. The composition of any one of claims 8 to 10 which further comprises a chromene compound.
12. The composition of claim 11 in which the chromene compound is represented by the following general formula [V]

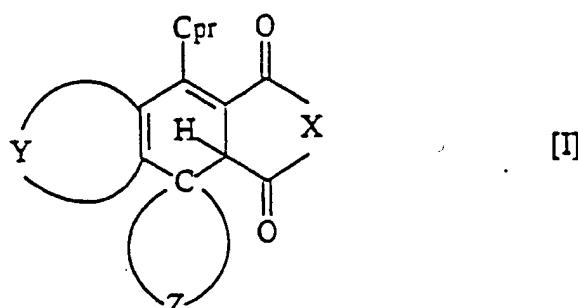


25 wherein R₁, R₂, R₃ and R₄ are the same or different, and each represents a hydrogen atom, an alkyl group, an aryl group, a substituted amino group or a saturated heterocyclic group, R₃ and R₄ may together form a ring, and the group Y is a divalent aromatic hydrocarbon group or a divalent unsaturated heterocyclic group each of which may optionally be substituted.

- 30
13. A photochromic lens comprising the composition of any one of claims 8 to 12.

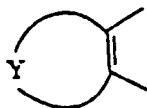
35 **Patentansprüche**

1. Verbindung der Formel (I)



45 worin

50

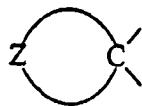


5

eine zweiwertige aromatische Kohlenwasserstoffgruppe oder eine zweiwertige ungesättigte heterocyclische Gruppe bedeutet, von denen jede gegebenenfalls durch ein Halogenatom, eine Nitrogruppe, eine Cyangruppe, eine Amingruppe, eine Alkylthiogruppe mit 1 bis 4 Kohlenstoffatomen, eine Arylgruppe mit 6 bis 10 Kohlenstoffatomen, eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen und eine Alkoxygruppe mit 1 bis 4 Kohlenstoffatomen substituiert sein kann;

10

15 Cpr eine Cyclopropylgruppe bedeutet, die gegebenenfalls durch ein Halogenatom, Nitrogruppe, Cyangruppe, Amingruppe, Alkylthiogruppe mit 1 bis 4 Kohlenstoffgruppen, Arylgruppe mit 6 bis 10 Kohlenstoffatomen, Alkylgruppe mit 1 bis 4 Kohlenstoffatomen oder Alkoxygruppe mit 1 bis 4 Kohlenstoffatomen substituiert sein kann;



20

25 eine Norbornylidengruppe, eine Bicyclo[3.3.1]nonylid oder eine Adamantylidengruppe bedeutet, von denen jede gegebenenfalls durch ein Halogenatom, eine Hydroxygruppe, eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen, Alkoxygruppe mit 1 bis 4 Kohlenstoffatomen, eine Alkoxycarbonylgruppe mit 2 bis 10 Kohlenstoffatomen, eine Aralkylgruppe mit 7 bis 9 Kohlenstoffatomen, oder eine Arylgruppe mit 6 bis 10 Kohlenstoffatomen substituiert sein kann; und

25

30 X ein Sauerstoffatom, die Gruppe >N-R₁₁, die Gruppe >N-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂, die Gruppe >N-A₃-A₄ oder die Gruppe >N-A₃-R₁₃ bedeutet, worin

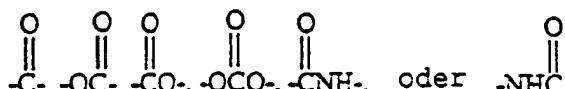
30

35 R₁₁ ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 20 Kohlenstoffatomen oder eine Arylgruppe mit 6 bis 10 Kohlenstoffatomen bedeutet,

35

A₁ und A₂ gleich oder verschieden sind und jeweils eine Alkylengruppe mit 1 bis 10 Kohlenstoffatomen, eine Alkylidengruppe mit 2 bis 10 Kohlenstoffatomen, eine Cycloalkylengruppe mit 3 bis 10 Kohlenstoffatomen oder eine Alkylcycloalkanediylgruppe mit 6 bis 10 Kohlenstoffatomen bedeutet,

35 B₁ und B₂ gleich oder verschieden sind und jeweils -O-,



40

bedeuten,

45 m und n unabhängig voneinander 0 oder 1 bedeuten, mit der Maßgabe, daß, wenn m 0 ist, n ebenfalls 0 ist, R₁₂ eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, eine Naphthylgruppe oder eine Naphthylalkylgruppe mit 1 bis 4 Kohlenstoffatomen in der Alkyleinheit, bedeutet, wobei die Alkylgruppe mit 1 bis 10 Kohlenstoffatomen gegebenenfalls durch 1 bis 3 Substituenten substituiert sein kann, die unabhängig voneinander ein Halogenatom, eine Cyangruppe oder Nitrogruppe sind, und die Naphthyl- oder Naphthylalkylgruppe gegebenenfalls durch 1 bis 3 Substituenten substituiert ist, die unabhängig voneinander ein Halogenatom, eine Cyangruppe, eine Nitrogruppe, eine Alkylaminogruppe mit 1 bis 3 Kohlenstoffatomen, eine Alkylgruppe mit 1 bis 3 Kohlenstoffatomen oder eine Alkoxygruppe mit 1 bis 3 Kohlenstoffatomen bedeuten,

45

50 A₃ eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, eine Alkylidengruppe mit 2 bis 10 Kohlenstoffatomen, eine Cycloalkylengruppe mit 3 bis 10 Kohlenstoffatomen, eine Alkylcycloalkanediylgruppe mit 6 bis 10 Kohlenstoffatomen bedeutet,

50

55 A₄ eine Naphthylgruppe bedeutet, die durch 1 bis 3 Substituenten substituiert sein kann, die unabhängig voneinander ein Halogenatom, eine Cyangruppe, eine Nitrogruppe, eine Alkylaminogruppe mit 1 bis 3 Kohlenstoffatomen, eine Alkylgruppe mit 1 bis 3 Kohlenstoffatomen oder eine Alkoxygruppe mit 1 bis 3 Kohlenstoffatomen sind, und

R_{13} ein Halogenatom, eine Cyangruppe oder eine Nitrogruppe bedeutet.

2. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß X die Gruppe $>N-A_3-R_{13}$ ist.
- 5 3. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß X die Gruppe $>N-A_1-B_1-(A_2)_m-(B_2)_n-R_{12}$ ist.
4. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß X die Gruppe $>N-A_3-A_4$ ist.
5. Verbindung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet,

10



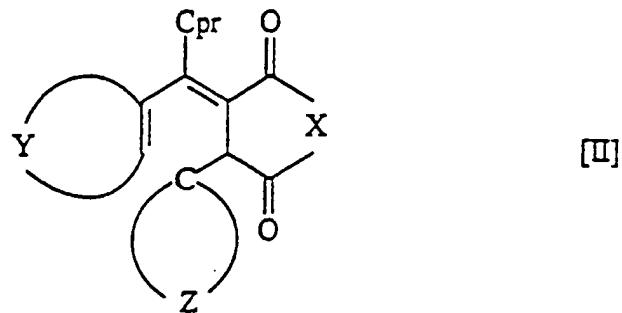
15

eine Arylgruppe mit 6 bis 14 Kohlenstoffatomen, eine 5- oder 6-gliedrige monocyclische Heterogruppe, die 1 bis 3 Stickstoff-, Sauerstoff- oder Schwefelatome enthält, oder eine kondensierte heterocyclische Gruppe bedeutet, die aus der Kondensation eines Benzol- oder Cyclohexenrings an die heterocyclische Gruppe resultiert, wobei jede durch 1 bis 3 Substituenten substituiert sein kann, die unabhängig voneinander ein Halogenatom, eine Nitrogruppe, eine Cyangruppe, eine iminogruppe, eine Alkylthiogruppe mit 1 bis 4 Kohlenstoffatomen, eine Arylgruppe mit 6 bis 10 Kohlenstoffatomen, eine alkylgruppe mit 1 bis 4 Kohlenstoffatomen oder eine Alkoxygruppe mit 1 bis 4 Kohlenstoffatomen bedeuten.

20

- 25 6. Verfahren zur Herstellung einer Verbindung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß es umfaßt das Cyclisieren einer Verbindung der Formel (II)

30



35

40

worin

45



50

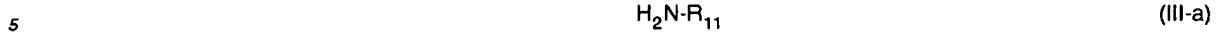
Cpr

55



EP 0 629 626 B1

und X die in Anspruch 1 angegebene Bedeutung besitzen, oder das Umsetzen der Verbindung der Formel (II), worin X ein Sauerstoffatom ist, mit einer Aminverbindung der Formel (III-a), (III-b), (III-c) oder (III-d)

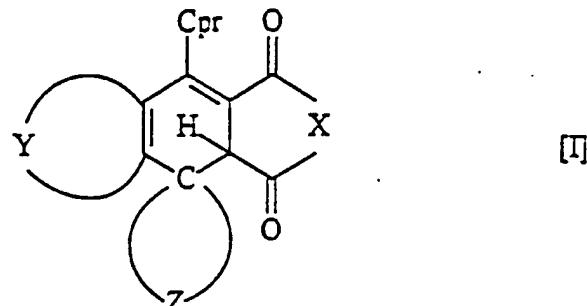


worin R_{11} , R_{12} , R_{13} , A_1 , A_2 , A_3 , A_4 , B_1 , B_2 , m und n die in Anspruch 1 angegebene Bedeutung besitzen,

und dann das Reaktionsprodukt cyclisiert.

20 7. Verfahren zur Herstellung einer Verbindung der Formel (I)

25

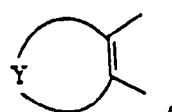


30

35

worin

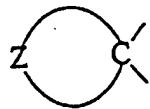
40



45

cpr

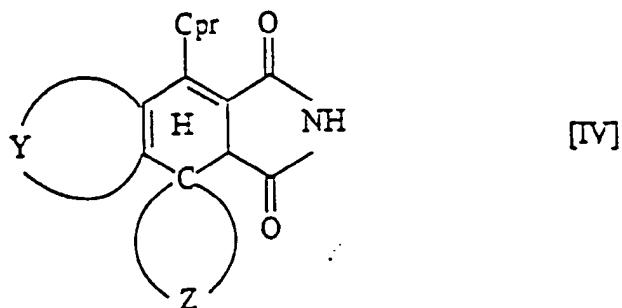
50



55

und X die in Anspruch 1 angegebene Bedeutung besitzen, mit der Maßgabe, daß X kein Sauerstoffatom ist, das umfaßt die Umsetzung einer Imidverbindung der Formel (IV)

5

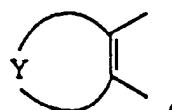


10

15

worin

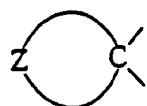
20



25

Cpr, und

30



35

Br-R₁₁

(V-a)

40

Br-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂

(V-b)

Br-A₃-A₄

(V-c)

45

Br-A₃-R₁₃

(V-d)

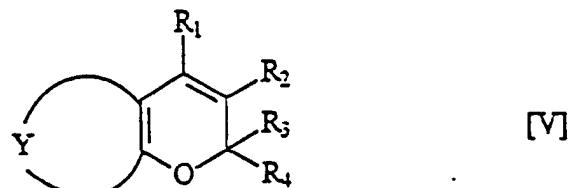
worin R₁₁, R₁₂, R₁₃, A₁, A₂, A₃, A₄, B₁, m und n die in Anspruch 1 angegebene Bedeutung besitzen.

50

8. Zusammensetzung, die ein Polymer mit hohem Molekulargewicht und eine in einem der Ansprüche 1 bis 8 beanspruchte Verbindung umfaßt.
9. Zusammensetzung nach Anspruch 8, dadurch gekennzeichnet, daß sie außerdem einen Ultraviolettschutzstabilisator umfaßt.
10. Zusammensetzung nach Anspruch 9, dadurch gekennzeichnet, daß der Ultraviolettschutzstabilisator ein Lichtlöscher für Sauerstoff im Singlett-Zustand oder ein gehindertes Amin-Lichtstabilisator ist.

11. Zusammensetzung nach einem der Ansprüche 8 bis 10, dadurch gekennzeichnet, daß sie außerdem eine Chromenverbindung umfaßt.

12. Zusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß die Chromenverbindung dargestellt wird durch die folgende allgemeine Formel (V)



20

worin R₁, R₂, R₃ und R₄ gleich oder verschieden sind und jeweils ein Wasserstoffatom, eine Alkylgruppe, eine Arylgruppe, eine substituierte Aminogruppe oder eine gesättigte heterocyclische Gruppe bedeuten, R₃ und R₄ zusammen einen Ring bilden können, und die Gruppe Y eine zweiwertige aromatische Kohlenwasserstoffgruppe oder eine zweiwertige ungesättigte heterocyclische Gruppe ist, von denen jede gegebenenfalls substituiert sein kann.

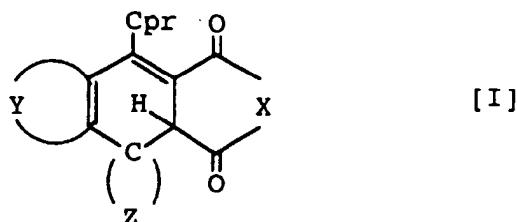
13. Photochrome Linse, die die Zusammensetzung nach einem der Ansprüche 8 bis 12 umfaßt.

25

Revendications

1. Composé de formule (I)

30



40

dans laquelle



50

représente un groupe hydrocarboné aromatique divalent ou un groupe hétérocyclique insaturé divalent, chacun d'eux pouvant éventuellement être substitué par un atome d'halogène, un groupe nitro, un groupe cyano, un groupe amino, un groupe alkylthio ayant 1 à 4 atomes de carbone, un groupe aryle ayant 6 à 10 atomes de carbone, un groupe alkyle ayant 1 à 4 atomes de carbone ou un groupe alcoxy ayant 1 à 4 atomes de carbone;

55

Cpr représente un groupe cyclopropyle qui peut éventuellement être substitué par un atome d'halogène, un groupe nitro, un groupe cyano, un groupe amino, un groupe alkylthio ayant 1 à 4 atomes de carbone, un groupe aryle ayant 6 à 10 atomes de carbone, un groupe alkyle ayant 1 à 4 atomes de carbone ou un groupe alcoxy ayant 1 à 4 atomes de carbone;



5

représente un groupe norbornylidène, un groupe bicyclo[3.3.1]nonylidène, ou un groupe adamantylidène, chacun d'eux pouvant éventuellement être substitué par un atome d'halogène, un groupe hydroxyle, un groupe alkyle ayant 1 à 4 atomes de carbone, un groupe alcoxy ayant 1 à 4 atomes de carbone, un groupe alcoxy-carbonyle ayant 2 à 10 atomes de carbone, un groupe aralkyle ayant 7 à 9 atomes de carbone ou un groupe aryle ayant 6 à 10 atomes de carbone; et

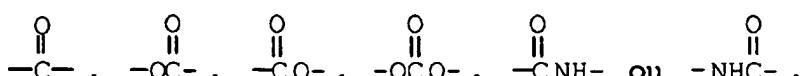
10 X représente un atome d'oxygène, le groupe $>N\text{-R}_{11}$, le groupe $>N\text{-A}_1\text{-B}_1\text{-(A}_2\text{)}_m\text{-(B}_2\text{)}_n\text{-R}_{12}$, le groupe $>N\text{-A}_3\text{-A}_4$, ou le groupe $>N\text{-A}_3\text{-R}_{13}$,

où

15 R_{11} représente un atome d'hydrogène, un groupe alkyle ayant 1 à 20 atomes de carbone, ou un groupe aryle ayant 6 à 10 atomes de carbone,

A_1 et A_2 sont identiques ou différents et représentent chacun un groupe alkylène ayant 1 à 10 atomes de carbone, un groupe alkylidène ayant 2 à 10 atomes de carbone, un groupe cycloalkylène ayant 3 à 10 atomes de carbone ou un groupe alkylcycloalcanediyle ayant 6 à 10 atomes de carbone,

20 B_1 et B_2 sont identiques ou différents, et représentent chacun $-\text{O}-$,



25

m et n, indépendamment les uns des autres, représentent 0 ou 1, pour autant que lorsque m vaut 0, n est aussi égal à 0,

20 R_{12} représente un groupe alkyle ayant 1 à 10 atomes de carbone, un groupe naphtyle ou un groupe naphtylalkyle ayant 1 à 4 atomes de carbone dans le fragment alkyle, le groupe alkyle ayant 1 à 10 atomes de carbone étant éventuellement substitué par 1 à 3 substituants qui sont chacun indépendamment un atome d'halogène, un groupe cyano ou un groupe nitro, et le groupe naphtyle ou naphtylalkyle étant éventuellement substitué par 1 à 3 substituants qui sont chacun indépendamment un atome d'halogène, un groupe cyano, un groupe nitro, un groupe alkylamino ayant 1 à 3 atomes de carbone, un groupe alkyle ayant 1 à 3 atomes de carbone ou un groupe alcoxy ayant 1 à 3 atomes de carbone,

35 A_3 représente un groupe alkylène ayant 1 à 10 atomes de carbone, un groupe alkylidène ayant 2 à 10 atomes de carbone, un groupe cycloalkylène ayant 3 à 10 atomes de carbone, ou un groupe alkylcycloalcanediyle ayant 6 à 10 atomes de carbone,

40 A_4 représente un groupe naphtyle qui peut être substitué par 1 à 3 substituants qui sont chacun indépendamment un atome d'halogène, un groupe cyano, un groupe nitro, un groupe alkylamino ayant 1 à 3 atomes de carbone, un groupe alkyle ayant 1 à 3 atomes de carbone ou un groupe alcoxy ayant 1 à 3 atomes de carbone, et

45 R_{13} représente un atome d'halogène, un groupe cyano ou un groupe nitro.

2.

Composé selon la revendication 1 dans lequel X est le groupe $>N\text{-A}_3\text{-R}_{13}$.

45

3. Composé selon la revendication 1 dans lequel X est le groupe $>N\text{-A}_1\text{-B}_1\text{-(A}_2\text{)}_m\text{-(B}_2\text{)}_n\text{-R}_{12}$.

4.

Composé selon la revendication 1 dans lequel X est le groupe $>N\text{-A}_3\text{-A}_4$.

50

5. Composé selon l'une quelconque des revendications 1 à 4 dans lequel



55

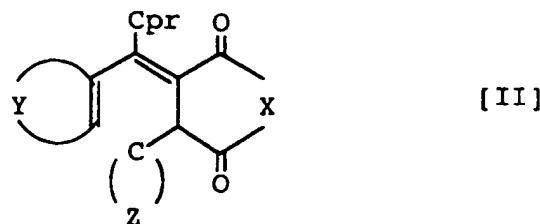
représente un groupe aryle ayant 6 à 14 atomes de carbone, un groupe hétéro-monocyclique à 5 ou 6 chaînons contenant 1 à 3 atomes d'azote, d'oxygène ou de soufre, ou un groupe hétérocyclique condensé résultant de la

condensation d'un noyau benzénique ou cyclohexénique avec le groupe hétérocyclique, chacun d'eux pouvant être substitué par 1 à 3 substituants qui sont chacun indépendamment un atome d'halogène, un groupe nitro, un groupe cyano, un groupe amino, un groupe alkylthio ayant 1 à 4 atomes de carbone, un groupe aryle ayant 6 à 10 atomes de carbone, un groupe alkyle ayant 1 à 4 atomes de carbone ou un groupe alkoxy ayant 1 à 4 atomes de carbone.

5

6. Procédé de préparation d'un composé selon l'une quelconque des revendications 1 à 5 qui comprend la cyclisation d'un composé de formule (II)

10



15

20 dans laquelle

25



Cpr

30



35

et X sont tels que définis dans la revendication 1,

ou la réaction du composé de formule (II) dans laquelle X est un atome d'oxygène avec un composé amine de formule [III-a], [III-b], [III-c] ou [III-d]



40



45

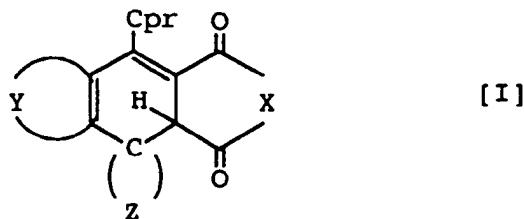


50

où R_{11} , R_{12} , R_{13} , A_1 , A_2 , A_3 , A_4 , B_1 , B_2 , m et n sont tels que définis dans la revendication 1,
puis la cyclisation du produit réactionnel.

55

7. Procédé de préparation d'un composé de formule [I]



10

dans laquelle



Cpr

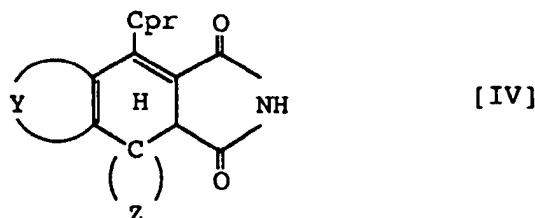
20



25

et X sont tels que définis dans la revendication 1, à condition que X ne soit pas un atome d'oxygène, qui comprend la réaction d'un composé imide de formule [IV]

30



dans laquelle

40



45 Cpr, et



sont tels que définis dans la revendication 1 avec un métal alcalin, puis la réaction du produit avec un composé de bromé de formule [V-a], [V-b], [V-c] ou [V-d]

55

Br-R₁₁

[V-a]

Br-A₁-B₁-(A₂)_m-(B₂)_n-R₁₂

[V-b]

5

Br-A₃-R₄

[V-c]

Br-A₃-R₁₃

[V-d]

10

dans lesquelles R₁₁, R₁₂, R₁₃, A₁, A₂, A₃, A₄, B₁, B₂, m et n sont tels que définis dans la revendication 1,

15

8. Composition comprenant un polymère de haut poids moléculaire et un composé selon l'une quelconque des revendications 1 à 5.

19

9. Composition selon la revendication 8 qui comprend en outre un stabilisant ultraviolet.

20

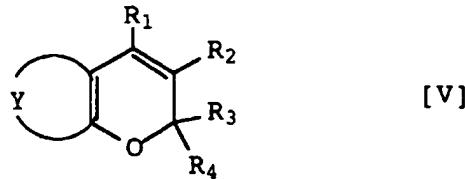
10. Composition selon la revendication 9 dans laquelle le stabilisant ultraviolet est un photoextincteur pour l'oxygène à l'état de singulett ou un photostabilisant de type amine encombrée.

11. Composition selon l'une quelconque des revendications 8 à 10 qui comprend en outre un composé de chromène.

12. Composition selon la revendication 11 dans laquelle le composé de chromène est représenté par la formule générale [V] suivante

25

30



35

dans laquelle R₁, R₂, R₃ et R₄ sont identiques ou différents, et représentent chacun un atome d'hydrogène, un groupe alkyle, un groupe aryle, un groupe amino substitué ou un groupe hétérocyclique saturé, R₃ et R₄ peuvent former ensemble un cycle, et le groupe Y est un groupe hydrocarboné aromatique divalent ou un groupe hétérocyclique insaturé divalent, chacun d'eux pouvant éventuellement être substitué.

40

13. Lentille photochromique comprenant la composition selon l'une quelconque des revendications 8 à 12.

45

50

55

FIG. 1

